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REMOVAL OF MANGANESE FROM MINE DRAINAGE BY OZONE AND CHLORINE

Ralph B. Rozelle, et al

Wilkes College

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REMOVAL OF MANGANESE FROM MINE DRAINAGE BY OZONE AND CHLORINE

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16. ABSTRACT

This research was directed toward an examination of methods by which coal mine water could be treated for removal of manganese. The objectives were to reduce manganese concentrations to at least 1 mg/l and preferably less than 0.05 mg/l. In order to remove manganese from mine water, strong oxidizers must be employed to oxidize it to the (+4) oxidation state in which it is relatively insoluble and will precipitate as MnO_2. Both ozone and hypochlorite ion were effective in this oxidation and reduced manganese concentrations to less than 1 mg/l and in some cases to less than 0.05 mg/l. Reaction orders based on initial reaction rates are reported for the manganese (II) at pH values of 2, 4, 6 and 7.9 in the time intervals studied. Solubilities of both manganese (II) hydroxide and manganese (IV) oxide were measured. Cost data were developed for both the ozone and sodium hypochlorite treatment.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Fresh water streams must be protected from untreated discharges, such as coal mine drainage, which can have adverse effects on the stream ecology.

Discharges from coal mines often contain high concentrations of manganese which is a heavy metal. When present in discharges, deleterious effects on both stream ecology and water supplies taken from streams may result. Research on this project determined chemical methods by which manganese could be reduced to concentrations which are acceptable for discharge into streams thus preventing water contamination.

This laboratory work is very preliminary in nature and requires further development and additional data in order to determine whether or not the findings are extendable into actual field work.

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ABSTRACT

This research was directed toward an examination of methods by which coal mine water could be treated for removal of manganese which is a transition metal. The objectives were to reduce manganese concentrations to at least 1 mg/l and preferably less than 0.05 mg/l. In order to remove manganese from mine water, strong oxidizers must be employed to oxidize it to the (+4) oxidation state in which it is relatively insoluble and will precipitate as MnO_2.

Both ozone and hypochlorite ion were effective in this oxidation and reduced manganese concentrations to less than 1 mg/l and in some cases to less than 0.05 mg/l. Reaction orders based on initial reaction rates are reported for the manganese (II) oxidation reaction with both of these oxidizing agents. Chlorine gas did not significantly oxidize manganese (II) at pH values of 2, 4, 6 and 7.9 in the time intervals studied. Solubilities of both manganese (II) hydroxide and manganese (IV) oxide were measured. The Solubility Product Constant for manganese (II) hydroxide was found to be 9×10^{-14}. The Equilibrium Constant for the solubility of manganese (IV) oxide was determined to be 4×10^{-5}.

Cost data were developed for both the ozone and sodium hypochlorite treatment. This report was submitted in fulfillment of Project R801236 by Wilkes College under the sponsorship of the Environmental Protection Agency.

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SECTION I

CONCLUSIONS

The following is a list of conclusions relevant to the removal of manganese from coal mine drainage:

I. Both ozone (O_3) and hypochlorite ion (OCl^-) are effective in the oxidation of soluble manganese (II) to an insoluble state (MnO_2) in which the concentration can be reduced to within acceptable limits (<1 ppm) for discharge into streams.

II. Fundamental reaction orders were found from initial reaction rates for the manganese (II)-ozone reaction. These were about 0.5 for manganese (II) at manganese (II) concentrations above 10 mg/l and 1.0 at concentrations below 10 mg/l. At low pH values the reaction is first order in ozone gas concentration over all concentration ranges studied. At higher pH values (~7) the reaction is about first order in ozone gas concentration at low concentrations (<10 mg/l O_2) and about 0.5 order for higher ozone gas concentrations (>10 mg/l O_2).

III. Fundamental reaction orders for the manganese (II)-hypochlorite reaction were determined to be 1.0 order for both manganese (II) and the hypochlorite ion.

IV. The solubility of $Mn(OH)_2$ was measured and the K_{sp} was calculated to be 9×10^{-14} at 25°C. The measured K_{eq} for the solubility of MnO_2 was found to be 4×10^{-5} at 25°C.

V. Chlorine gas did not oxidize manganese (II) to manganese (IV) at pH values of 2, 4, 6 or 7.9.

VI. Manganese was reduced to lower concentrations (<0.05 ppm) in solutions around a pH of 7 than at lower pH values when treated with ozone.

VII. Cost analysis indicates sodium hypochlorite solution would be more economical to use for treatment of coal mine drainage with low manganese concentrations and low volume discharges, whereas, ozone is more economical when the mine drainage contains higher manganese (II) concentrations and higher volume discharges.

SECTION II

RECOMMENDATIONS

A research-stage treatment technology has been developed in this experimental work for removal of manganese from coal mine drainage discharges and other waters through application of ozone gas and sodium hypochlorite solution. It is recommended that both of these treatment methods be scaled up to the pilot-plant stage for further investigation of the treatment processes which appear promising.

SECTION III

INTRODUCTION

GENERAL

Pollution of fresh water streams with coal mine drainage has become an increasingly prominent problem in recent years. Mine drainage results from water which accumulates in mines and may contain a number of contaminants which cause water pollution. The most recognized pollutants are iron, acid and sulfate which result from the bacterial oxidation of pyrite (FeS_x) in mines. The water in mines is generally highly acidic having a low pH (2-4) and is referred to as acid mine drainage (AMD).

Very often coal mine water will contain significant amounts of other metals. One of these metals is a transition metal, manganese, which can be present in significant amounts and is usually present in the (+2) oxidation state.

When coal mine water enters a stream, manganese (II) appears to undergo oxidation to an insoluble manganese (IV) oxide (MnO_2). Presumably the oxidizing and hydrolyzing reaction would be similar to:

$$Mn^{+2} + H_2O + 1/2\ O_2 = MnO_2 + 2H^+$$

which would have the effect of producing acid as well as insoluble MnO_2. MnO_2 can have deleterious effects on both stream ecology, through deposit on the stream bed, and on downstream water consumers, by clogging filters. Therefore, it is important to develop treatment methods by which manganese can be removed from coal mine water.

Examples of manganese and iron concentrations present in mine water from anthracite mines in the Wyoming Valley of Northeastern Pennsylvania are shown in Table 1.

Table 1. ANALYSES OF MINE WATERS IN WYOMING VALLEY, PENNSYLVANIA

	pH	Fe ppm	Mn ppm
Discharge I	3.4	295	22
Discharge II	5.8	153	10.6
*Culm Runoff	2.5	1044	83.2

* Note -- Culm bank runoff is especially high in manganese concentration.

STATE OF TREATMENT TECHNOLOGY FOR MINE DRAINAGE

Large scale treatment methods used for treatment of coal mine drainage are designed primarily to remove iron and acid from the water. These are chemical methods which typically involve neutralization with lime or limestone followed by an aeration step to oxidize iron (II) (ferrous iron) to iron (III) (ferric iron) according to a reaction similar to:

$$2\ Fe^{+2} + 2H^{+} + 1/2\ O_2 = 2\ Fe^{+3} + H_2O$$

followed by a hydrolysis reaction:

$$Fe^{+3} + 3H_2O = Fe\ (OH)_3 + 3H^{+}$$

in which $Fe\ (OH)_3$ may appear as a hydrated oxide or a basic sulfate which is commonly referred to as "yellow boy."

Adjustments of pH in the first reaction are usually to 7 or slightly higher.

This neutralization-aeration process provides a successful treatment for removal of iron and acid, but does not reduce manganese concentrations to acceptable levels. Acceptable manganese concentration levels are less than 1 mg/l. However, a preferred level is less than 0.05 mg/l which is the upper limit for potable water.

The reasons that the neutralization-aeration process does not reduce manganese (II) concentrations to acceptable levels are two-fold:

I. Oxygen in water involved in the aeration process is not a strong enough oxidizing agent under these conditions to oxidize manganese (II) to manganese (IV) and remove manganese as MnO_2.

II. $Mn(OH)_2$ is more soluble than $Fe(OH)_3$ and will not precipitate as $Fe(OH)_3$ does from neutral or near neutral solutions.

The solubility product constant (K_{sp}) for $Mn(OH)_2$ is approximately 1×10^{-13}. Hence

$$1 \times 10^{-13} = K_{sp} = (Mn^{+2}) \quad (OH^-)^2$$

where (Mn^{+2}) and (OH^-) represent the molar concentrations of manganese (II) and hydroxyl ion, respectively, which are in a saturated solution if ideal behavior is assumed, i.e., the activities of all species are approximated by their concentrations. Using the solubility product equation above and assuming various hydroxyl ion concentrations, the concentrations of manganese (II) in saturated solutions of $Mn(OH)_2$ can be calculated as a function of hydroxyl ion concentration and pH. Results of these calculations are given in Table 2 which shows the manganese (II) concentrations in saturated solutions as a function of pH.

Table 2. MANGANESE (II) CONCENTRATIONS IN SATURATED SOLUTIONS vs. pH

pH	Manganese (II) Concentrations in a Saturated Solution mg/l
7	5.5×10^{5}
8	5.5×10^{3}
9	5.5×10^{1}
10	5.5×10^{-1}
11	5.5×10^{-3}

As demonstrated in Table 2, in a neutralization treatment process, a pH of 10 would be required to reduce the manganese concentration to less than 1 mg/l and a pH of 11 to reduce it below the potable water limit of 0.05 mg/l. Hence, considerable over-neutralization would be required to treat coal mine water for manganese removal if a neutralization-aeration process were used.

Newer treatment methods such as reverse osmosis (RO), which are designed to produce potable water, do not reduce the concentration of manganese to within potable limits (< 0.05 mg/l).

INVESTIGATIONS

The following investigations were made:

I. Reaction of ozone and manganese (II), because ozone is a strong oxidizing agent and should oxidize manganese (II) to manganese (IV).

II. Reactions of sodium hypochlorite and chlorine gas with manganese (II) to determine whether these oxidizing agents would oxidize manganese (II) to manganese (IV).

III. Reactions of ozone and sodium hypochlorite on acid mine drainage to determine the effects of these oxidizers on reactions with manganese (II) and iron (II).

IV. Solubility studies on $Mn(OH)_2$ and MnO_2 because the solubilities as a function of pH will determine the manganese concentrations which can remain in solution and affect the treatment process.

V. Cost studies on the use of both ozone and sodium hypochlorite for treatment of coal mine drainage for removal of manganese.

THEORY OF OXIDATION

In order to remove manganese from coal mine drainage a strong oxidizing agent is required to oxidize manganese (II) to manganese (IV). In the latter state it will hydrolyze and produce insoluble MnO_2.

The ease with which a particular chemical reactant is oxidized is a function of the electrochemical potential of the half-cell reaction. For the oxidation of manganese (II) to manganese (IV), the half-cell reaction and standard state electrochemical potential (E^o) in acid solution with reactants and products at unit activity is:

$$MnO_2 + 4H^+ + 2e^- = Mn^{+2} + 2H_2O \qquad E^o = +1.23v$$

The electrochemical potential (E) varies as a function of the activities of the reactants and products as demonstrated in the Nernst equation,

$$E = E^o - \frac{RT}{nF} \ln \frac{a_{Mn^{+2}} \, a_{H_2O}^2}{a_{MnO_2} \, a_{H^+}^4}$$

where E represents the electrochemical potential, E^o is the electrochemical potential under standard state conditions, R is the ideal gas constant, T is the temperature in degrees Kelvin, n is the number of electron equivalents per mole of Mn^{+2}, F is the Faraday and is equal to 23.060 Kcal/volt-equivalent and the a's represent the activities of the reactants and products as labeled.

The standard state potential of the ozone -oxygen couple is:

$$2e^- + O_3 + 2H^+ = O_2 + H_2O \qquad E^o = +2.07v$$

Thus, for the reaction of O_3 and Mn^{+2} under standard state conditions,

$$O_3 + Mn^{+2} + H_2O = O_2 + MnO_2 + 2H^+$$

The standard state potential (E^o) at a pH of 0 is 2.07 - 1.23 = 0.84v. The standard state energy change, ΔG^o, is related to the standard state potential by:

$$\Delta G^o = -nFE^o$$

A positive value for the potential produces a negative standard state free energy change. A negative standard state free energy change indicates that the reaction will proceed spontaneously, in terms of thermodynamics, and is often used as an initial measure of whether a reaction will proceed or not.

In the reaction of ozone and manganese (II) considered in this work, the reactants and products are not at unit activities. Hence, the electrochemical potential will not be E^o but some other value (E) determined by the Nernst equation and the activities of the reactants and products under the conditions being investigated. However, because the standard state electrochemical potential (E^o) is numerically very large, it is assumed that it will remain positive under the conditions which would be encountered in water treatment, i.e. under conditions of activities of reactants and products other than one and at different temperatures.

SECTION IV

EXPERIMENTAL DESIGN

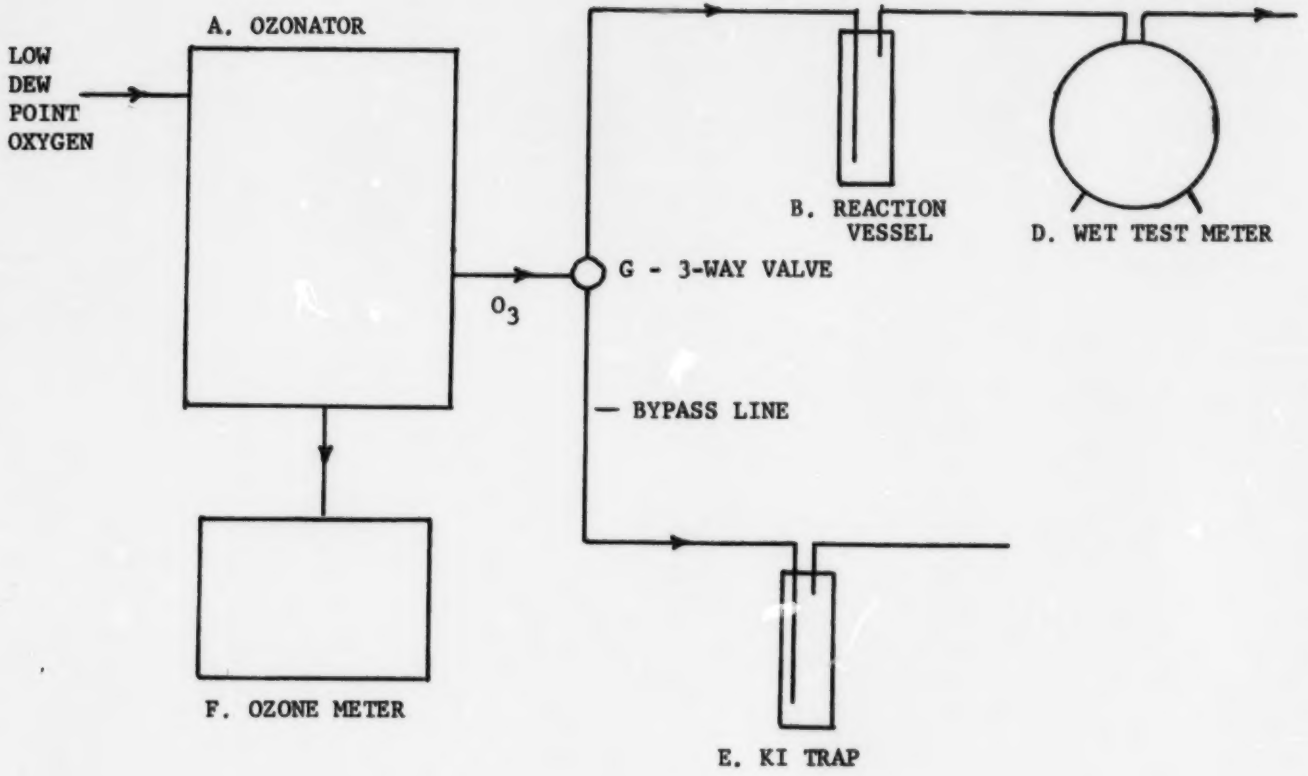
KINETIC STUDIES

Reaction kinetic studies were carried out in a static system. A Welsbach T-23 laboratory generator, (A), shown in Figure 1, generated ozone which was directed through a reaction vessel, (B) or through a by-pass line (E). The reaction vessel consisted of a 500 ml suction flask containing a known volume of manganese (II), acid mine drainage, or other solution under investigation, at a known pH and temperature. Sometimes the solution contained known amounts of other ions in order to study the effect of their presence on reaction rates. The synthetic solutions were prepared from reagent grade $MnSO_4 \cdot H_2O$ and other reagent grade chemicals as desired.

The flow rate and concentration of ozone were measured using a calibrated wet test meter (D) and a potassium iodide trap (E). The latter was titrated after a run for free iodine, using standardized sodium thiosulfate titrant, to determine the concentration of ozone that had passed through the line. Manganese concentrations were determined using a model 290 Perkin-Elmer AA spectrometer or a Fisher Atomsorb, model Ja 82-270-AA spectrometer.

Several sets of data were obtained using both the DB spectrometer and the AA spectrometer to analyze for manganese. The AA results agreed with those obtained by the DB when MnO_4^- solutions were used to calibrate the DB. However, DB results tended to run about 25% lower than AA results when the DB was calibrated using solutions of $MnSO_4 \cdot H_2O$ oxidized to permanganate using the periodate method. Iron (II) concentrations were determined by means of a Beckman DB spectrometer using the phenanthroline complex, absorption line at 510 mμ. Total iron was determined using the above described AA spectrometers. Twenty milliliter aliquots were removed at various time intervals during the reaction, filtered through a 50 mμ

Figure 1. Schematic diagram of ozonation system.



millipore filter to remove any precipitate, and analyzed. Except for the studies where the temperature was intentionally varied, a constant temperature bath was not employed and reaction temperatures were 25± 2°C.

SOLUBILITY STUDIES

The $Mn(OH)_2$ solubility studies were carried out as shown in Figure 2. The solutions containing solid $Mn(OH)_2$ were kept under CO_2 - free nitrogen in a constant temperature bath, 25.0± 0.1°C. The pH was carefully regulated using standard buffer solutions.[1] After various periods of equilibration to assure saturation by Mn^{+2} and OH^-, samples were removed, filtered through a 50 mμ millipore filter and analyzed by means of one of the same spectrometer methods used in the kinetic studies.

The MnO_2 solubility studies were also carried out under CO_2 - free N_2 at known buffered pH solutions (Table 3) in the apparatus shown in Figure 3.

Table 3. PREPARATION OF BUFFER SOLUTIONS

cc 0.1 M NaOH	cc (0.1 M H_3BO_3 + 0.1 M KCl)	Final Vol.	pH
109.2	125	250	10.0
52.0	125	250	9.0
9.8	125	250	8.0

The MnO_2 was washed with distilled water and filtered before use to remove soluble impurities. The MnO_2 was then placed in the solution of desired pH and the solution allowed to saturate with the soluble species of manganese (IV). Following equilibration samples were drawn-off and filtered through a millipore 50 mμ filter to remove any manganese containing solid. The solutions were subsequently analyzed for manganese on the Perkin Elmer 290 AA spectrometer.

MnO_2 solubility was studied at room temperature, 25°C, ± 2°, as a function of pH.

Figure 2. Apparatus for solubility measurements of $Mn(OH)_2$.

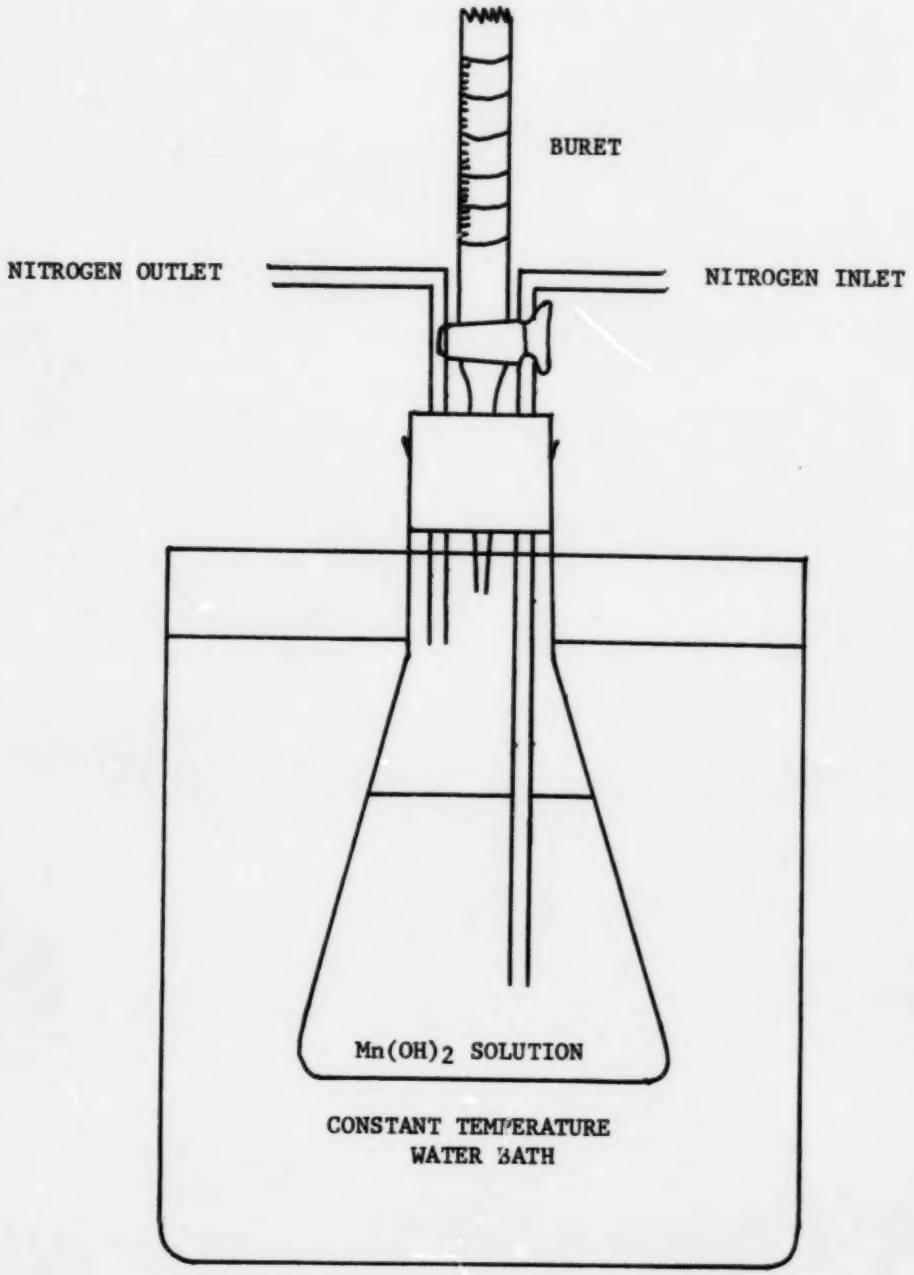
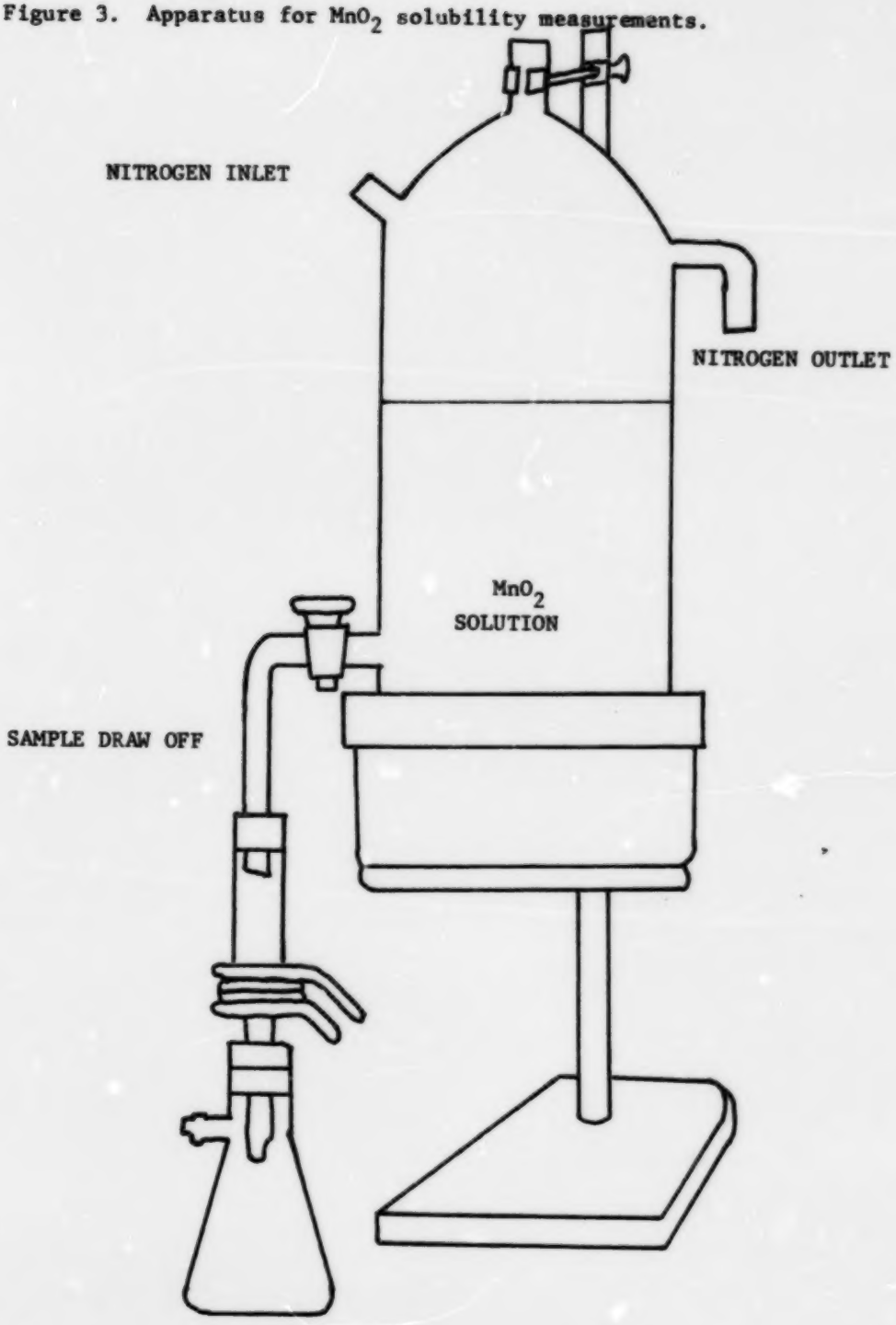


Figure 3. Apparatus for MnO_2 solubility measurements.



SECTION V

DISCUSSION OF RESULTS

KINETICS OF MANGANESE (II) - OZONE REACTION

General

The overall chemical reaction for the oxidation of manganese (II) can be written:

$$Mn^{+2} + O_3 + H_2O = MnO_2 + O_2 + 2H^+ \qquad (1.)$$

The rate expression for the oxidation by ozone gas can therefore be written

$$\text{rate} = k\ (Mn^{+2})^a\ (O_3\ (g)\ )^b \qquad (2.)$$

where a and b represent the reaction orders for manganese (II) and ozone, respectively, and k is the overall specific reaction rate constant. The concentration of water in the solutions studies in this work is essentially constant and is assumed to not contribute to the reaction rate substantially.

In complex chemical reactions, particularly those involving two phases, reaction orders are difficult to determine. In such cases, initial reaction rates often provide information on the reaction rate before significant chemical changes in the system have occurred. Measurement of initial reaction rates eliminates complications in reaction rate interpretations which may occur due to build up of product concentrations and large changes in the concentrations of reactants.

Manganese (II) Dependence of Reaction Rate

In the case of the manganese (II) -ozone reaction, the concentration of ozone in the gas-phase (O_3 (g)) was first kept constant and the

reaction rate measured at different manganese (II) concentrations. In this manner, reaction rates were measured at 2, 10, and 35 mg/l O_2 ozone gas-phase concentrations. The result of these measurements are shown in Figures 4 and 5 where the initial reaction rate is shown as a function of initial manganese (II) concentrations, at the 3 different constant ozone gas-phase concentrations. In each of the 3 curves, the reaction is shown to be about first order in initial manganese (II) concentration at manganese (II) concentrations of less than about 10 mg/l, but gradually changes to about 0.5 order above 10 mg/l initial manganese (II) concentrations. The results shown in Figure 5 were measured at a lower pH than those of Figure 4, but the same basic phenomenon was observed - First order changing to about 0.5 order in manganese (II) concentration as the initial manganese (II) concentration increased.

Ozone Dependence of Reaction Rate

Next, the initial concentration of manganese (II) was held constant and the ozone gas-phase concentration varied. Four sets of data from these measurements are plotted in Figures 6 and 7. In Figure 6 the initial manganese (II) concentration was 15 mg/l. The data supporting the curves were measured at different pH values. In Figure 7 the initial manganese (II) concentration was 30 mg/l and curves are again shown for two different pH values. At the higher pH values, the reaction rate was observed to be first order in ozone gas-phase concentration at low ozone concentrations of less than 10 mg/l. The rate subsequently changed to 0.5 order at the higher ozone concentrations (>10 mg/l). In the lower pH ranges, the reaction is about first order in ozone gas-phase concentration at all ozone concentrations studied.

Reaction Rate Dependence on pH

In Figures 6 and 7, the effect of pH on the reaction rate is shown. The reaction rate at pH 7-8 is about 2-3 times that at pH 3-5, a relatively small effect. Although there is a small pH effect, this effect appears to be indirect as will be discussed in more detail later.

Temperature Dependence of Reaction Rate

The dependency of the rate of reaction on temperature was studied using initial reaction rates. The data, which are given in Table 4 and Figure 8 indicate that the reaction rate is independent of temperature in the range - 2°C to 56°C.

Figure 4. Initial rate of the manganese (II) - ozonation reaction vs. various manganese (II) concentrations at a pH of 7-8.

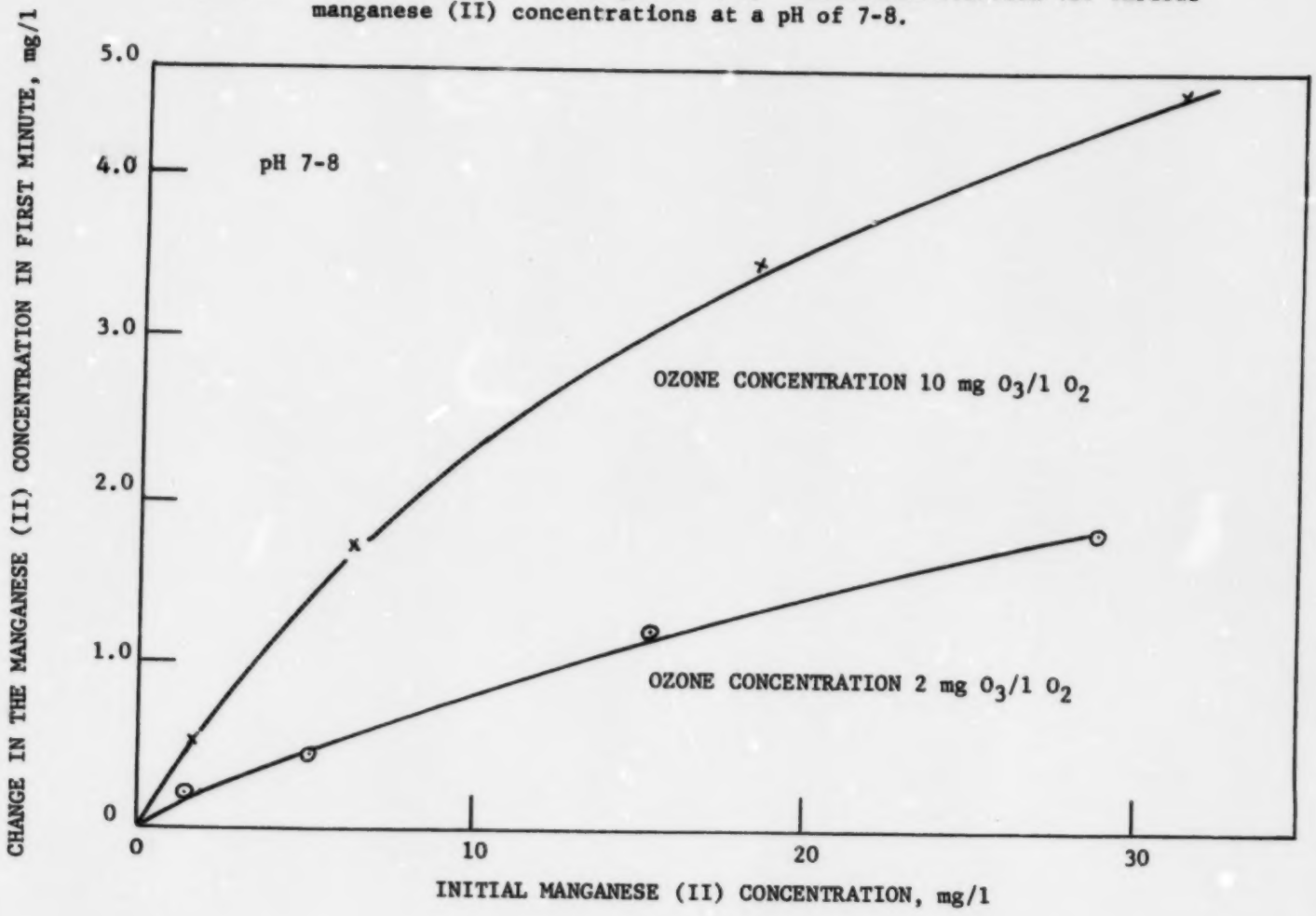


Figure 5. Initial rate of the ozone-manganese (II) reaction vs. initial manganese (II) concentration at a pH of 3-5.

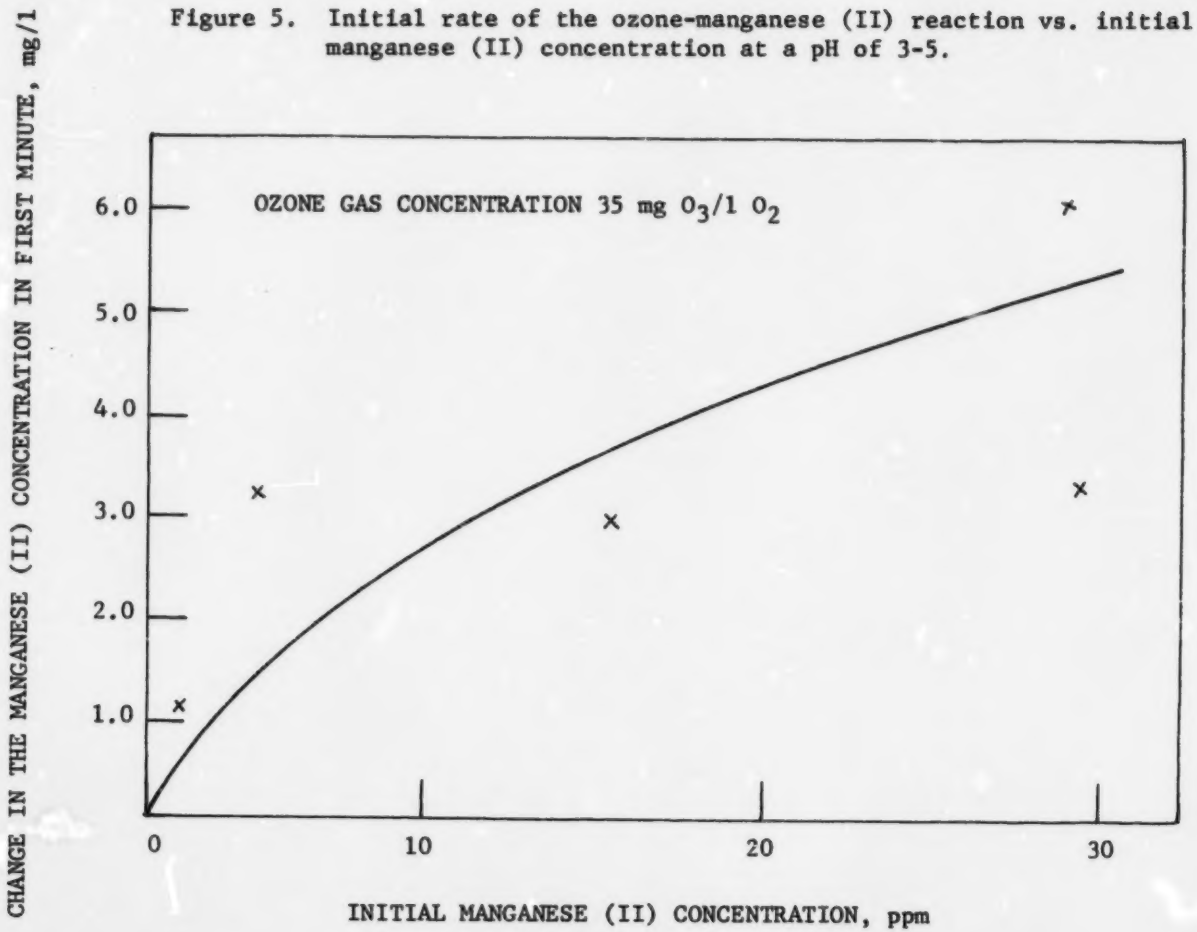


Figure 6. Initial rate of ozone-manganese (II) reaction vs. different ozone gas influent concentrations.

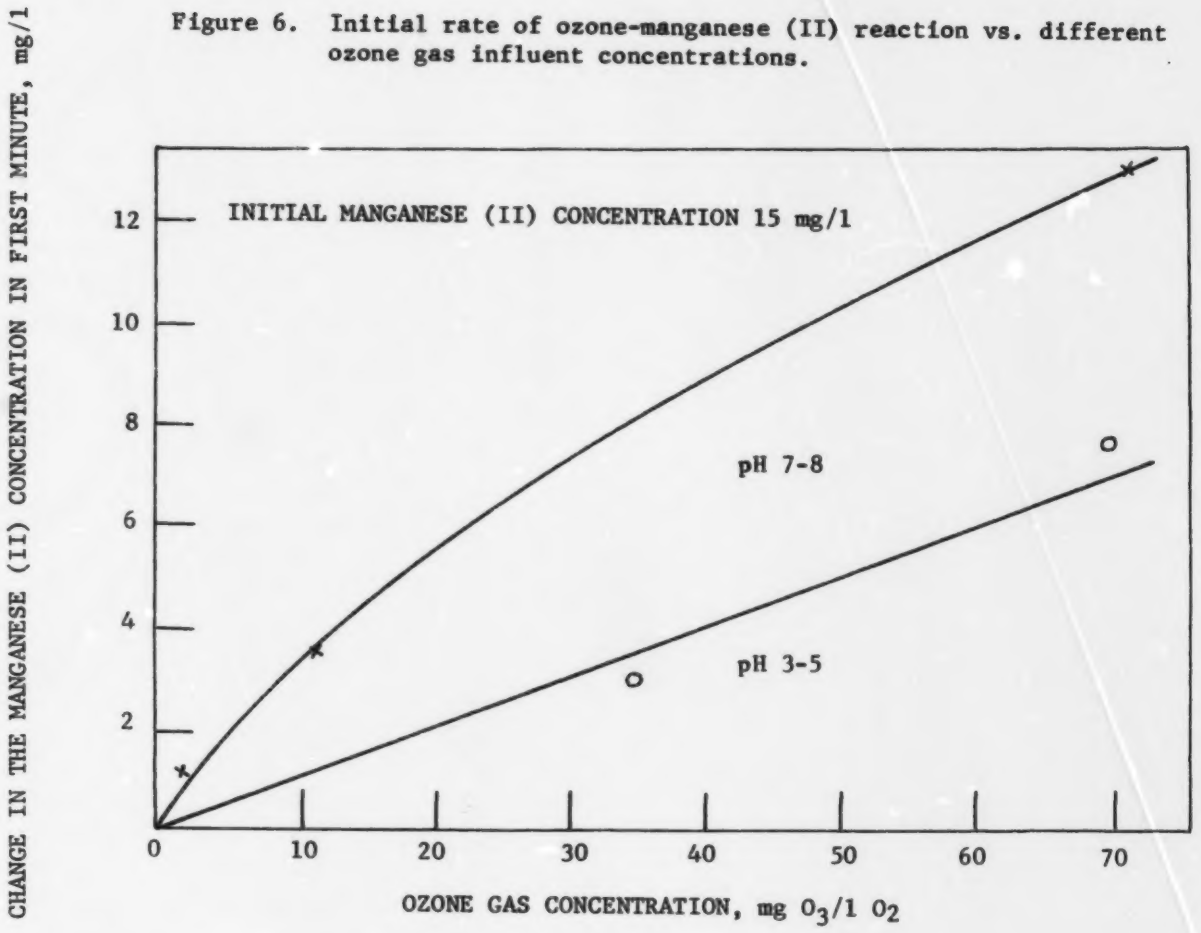


Figure 7. Initial rate of ozone gas-manganese (II) reaction vs. ozone gas influent concentration.

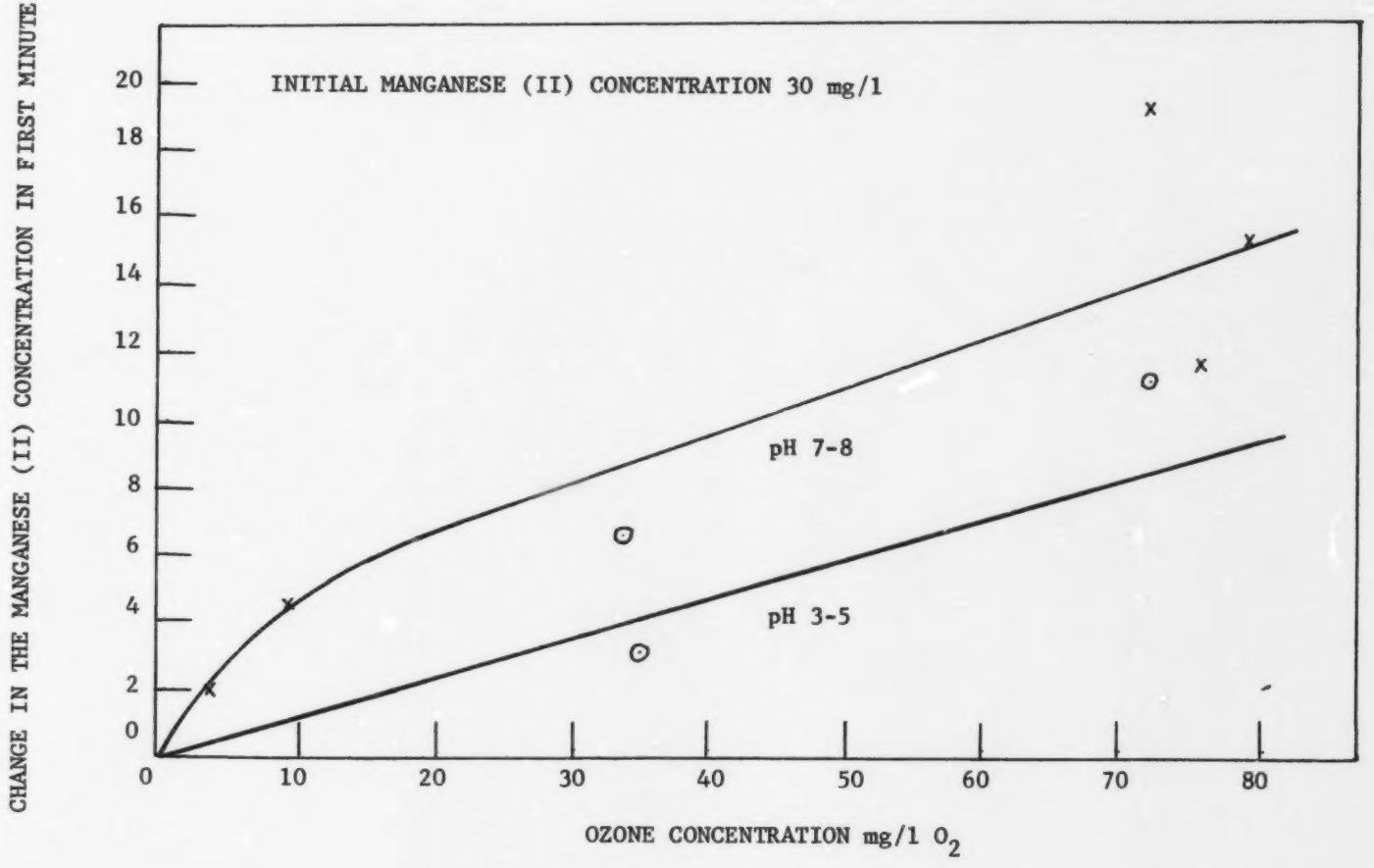


Figure 8. Initial rates of reaction of ozone-manganese (II) vs. initial manganese (II) concentration at various temperatures

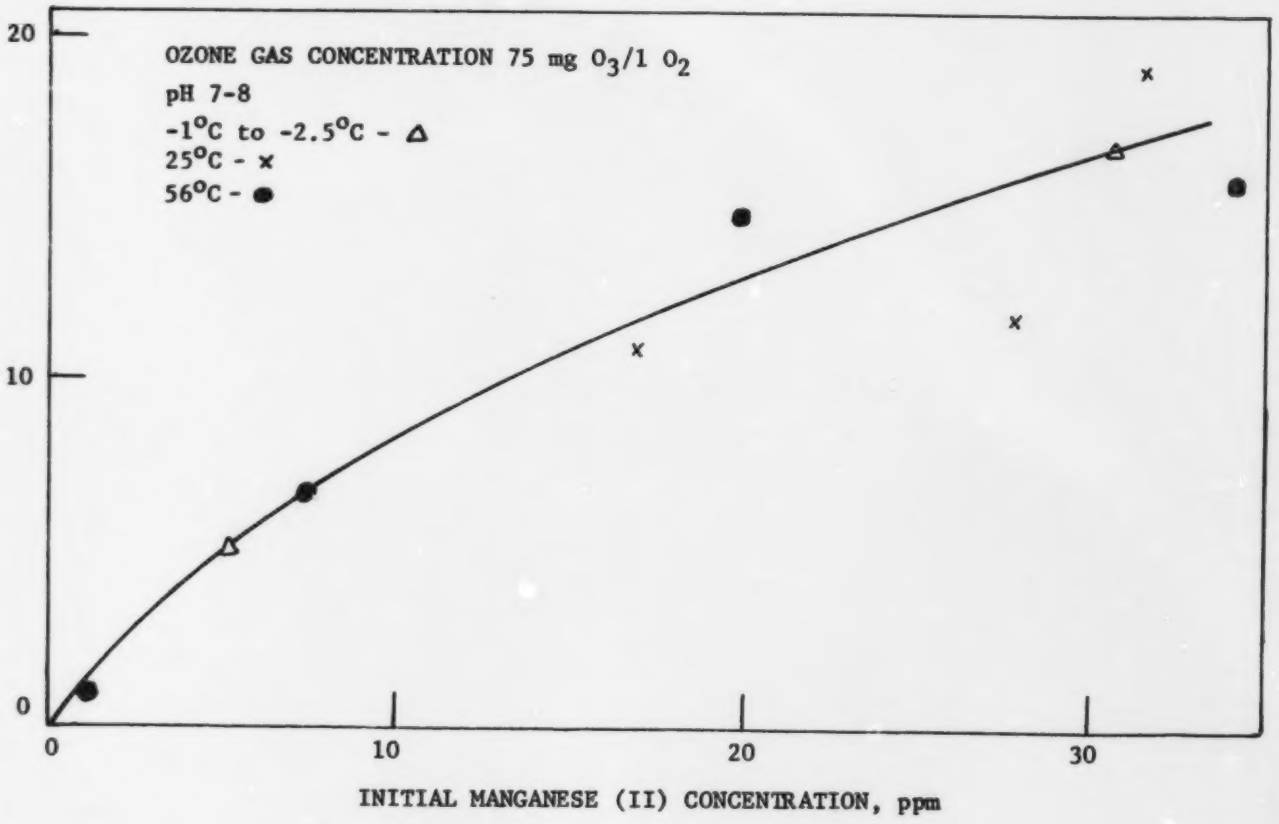


Table 4. KINETICS DATA ON RUNS IN WHICH THE TEMPERATURE WAS VARIED

Initial (Mn^{+2}) ppm	pH	O_3 mg/l O_2	Initial Rate ppm (Mn^{+2})/min.	T ^oC
34.2	8.0	74	15.6	56
20.0	7.9	74	14.7	56
7.5	8.2	75	6.7	56
1.2	7.9	75	0.8	56
30.6	8.0	77	16.8	-2.5
15.0	8.2	80	15	-1.0
5.3	8.0	78	5.1	-1.0
1.2	8.1	75	1.1	-1.0

This leads to a calculated zero activation energy for the reaction, a result which is reasonable for chemical reactions involving a very active species, such as ozone.

PROPOSED REACTION MECHANISM FOR THE MANGANESE (II) -OZONE REACTION

Considering the observed reaction orders, the following mechanism is proposed to explain the kinetics of the ozonation of manganese (II). The reaction of ozone with manganese (II) can be hypothesized to take place in two steps. One step involves the dissolution of ozone gas in the solution; the second step being the reaction of dissolved ozone with manganese (II) as shown in equation (3)

$$O_3\ (g) \underset{k_{-1}\ (1\ -\ \theta)}{\overset{k_1\ \theta}{\rightleftharpoons}} O_3\ (aq) \xrightarrow{k_2\ C_{Mn^{+2}}} MnO_2 \qquad (3.)$$

In Equation (3), gaseous ozone O_3 (g) at concentration $C_{O_3\ (g)}$ dissolves from a bubble into solution giving O_3 (aq) at a concentration $C_{O_3\ (aq)}$ which depends on the ozone gas concentration in the input oxygen stream. Some of the dissolved O_3 (aq) in turn can return to the gas phase via the reverse reaction. The rate constant for the dissolving process is equal to $k_1\ \theta$, where θ is the effective fraction of the volume of the water <u>not</u> saturated with aqueous dissolved O_3. The larger θ is, the faster the dissolving process can occur. When θ is held constant, the rate constant for this process is k_1; i.e., when the pressure of the gaseous ozone is held constant,

θ would be expected to be a constant value for that set of experiments. When the partial pressure of the ozone in the gas stream is lowered, θ would be expected to be larger as less water around the bubble will be saturated at any given instant.

Similarly, the rate at which dissolved ozone returns to bubble form will be k_{-1} $(1-\theta)$, where $(1-\theta)$ is the fraction of the water in the vicinity of the bubble that is saturated with ozone. The factor $(1-\theta)$ takes into account only the effect of local concentrations around the bubbles on the rate of return of ozone to the bubble form. The last step in the reaction in Equation (3) is that of the reaction of dissolved ozone, O_3 (aq), with manganese (II) ions to form MnO_2.

A steady-state is assumed to exist for any concentration of O_3 (aq); that is, the concentration of dissolved ozone reaches a constant value very quickly, compared to the rate of the overall ozonation reaction. This steady-state value approaches the maximum value that can be attained in saturated aqueous ozone solutions. In this steady-state, the concentration of dissolved ozone, O_3 (aq), is constant and its rate of change is, therefore, equal to zero and can be equated to the rates of the reactions. This is stated in Equation (4):

$$\frac{dC_{O_3\ (aq)}}{dt} = 0 = k_1\theta C_{O_3\ (g)} - k_{-1}\ (1-\theta)\ C_{O_3\ (aq)} - k_2 C_{Mn^{+2}}\ C_{O_3\ (aq)} \qquad (4.)$$

Hence,

$$C_{O_3\ (aq)} = \frac{k_{-1}\theta\ C_{O_3\ (g)}}{k_{-1}\ (1-\theta) + k_2 C_{Mn^{+2}}} \qquad (5.)$$

Therefore, the overall rate of the ozonation of manganese (II) is given as:

$$\text{rate} = k_2 C_{Mn^{+2}}\ C_{O_3\ (aq)} = \frac{k_2 k_1\ \theta C_{O_3\ (g)}\ C_{Mn^{+2}}}{k_{-1}\ (1-\theta) + k_2\ C_{Mn^{+2}}} \qquad (6.)$$

Equation (6), which is the quantitative statement of this proposed mechanism, will be used to explain the observed kinetics of the manganese (II)-ozone reaction, shown in Figures 4, 5, 6, and 7.

When the (initial) manganese (II) concentration is very small, the second term in the denominator of Equation (6) can be neglected with reference to the first and the equation reduces to:

$$\text{rate} = \frac{k_2 k_1 \theta C_{O_3\,(g)}\, C_{Mn^{+2}}}{k_{-1}\,(1-\theta)} \qquad (7)$$

which is in a form where a first order mechanism for $C_{Mn^{+2}}$ would be observed, and is in agreement with the observed results.

As the concentration of manganese (II) ($C_{Mn^{+2}}$) increases, the second term in the denominator can no longer be neglected, and the complete Equation (6) must be used to explain the kinetics; this leads to a fractional order dependence of the reaction rate on $C_{Mn^{+2}}$, again in agreement with the data.

The relative value of θ at various pH values and at various ozone gas-phase concentrations is the significant factor needed to explain the order of the reaction with regard to $O_3(g)$. The value of θ, the fraction of the volume of solution surrounding the $O_3(g)$ bubbles <u>not</u> saturated with $O_3(aq)$, tends to decrease as $C_{O_3(g)}$ increases; this occurs because as $C_{O_3(g)}$ increases, more $O_3(g)$ dissolves, and θ is thereby reduced.

The value of θ is also increased as the pH increases - causing the relatively small pH effect shown in Figures 6 and 7. At higher pH values, more base-catalyzed decomposition of ozone occurs, and less $O_3(aq)$ remains in solution, again increasing θ.

Therefore, at low pH's, θ is small, and the reaction rate is smaller than when the pH and θ are greater. Further, when the pH is low, θ is very small, approaching that of a saturated solution of $O_3(aq)$, and thereby remains effectively constant. When θ is constant, Equation (6) predicts a first order $O_3(g)$ concentration dependence at all values of $C_{O_3(g)}$ if $C_{Mn^{+2}}$ is maintained constant. Alternatively, when the pH is higher, θ is relatively large. When this is so, θ decreases as $C_{O_3(g)}$ increases giving a complex order for the $C_{O_3(g)}$ dependence in Equation (6). When $C_{O_3(g)}$ becomes greater, θ is smaller, $(1-\theta)$ is larger and Equation (6) predicts a fractional order dependence on $C_{O_3(g)}$. On the other hand, when $C_{O_3(g)}$ is very small, θ is large, $1-\theta$ is small and Equation (6) simplifies to that of a higher order reaction dependence on $C_{O_3(g)}$. These observations support the data on reaction orders found experimentally for ozone.

KINETICS OF OZONATION OF IRON (II)

Ozonation kinetics of iron (II) were studied over a range of initial iron (II) concentrations ranging from 10 mg/1 to 1000 mg/1. These were studied partially as a check on previous work done on the same ozonation system used in the manganese studies. The data are shown in Table 5 and Figures 9 and 10.

Table 5. KINETICS DATA FOR THE IRON (II) - OZONE REACTION

Initial (Fe^{+2}) ppm	pH	(O_3) mg/1 O_2	Initial Rate ppm Fe^{+2}/min
932	3	33	59
732	3	33	75
188	3	32	25
84	3.5	108	28
34	4	94	21
8.1	4	96	5.9
2.8	4	93	1.3

At higher iron (II) concentrations of between 30-1000 mg/1 the reaction rate was found to be zero order with respect to the iron (II) concentration. This result confirmed earlier results of Simpson.[2] Below about 30 mg/1 iron (II) the reaction appears to be first order in iron (II).

All runs were carried out at pH = 3.4 to assure that all of the iron (II) would remain in solution and not precipitate as iron (II) hydroxide. Since iron (III) hydroxide has a solubility product constant which is 1×10^{-36}, $Fe(OH)_3$ will precipitate at this pH with only a very small amount of iron (III) remaining in solution.

GENERAL DISCUSSION OF MANGANESE (II) OZONATION AND TREATMENT

It was demonstrated earlier that when manganese (II) solutions were ozonated the concentration of manganese (II) decreased according to a measured initial reaction rate which depends on the concentrations of the reacting species and the pH. The results in Figures 11 and 12 show that there is little problem in reducing the manganese con-

Figure 9. Initial rates of ozonation of iron (II) as a function of initial concentration of iron (II).

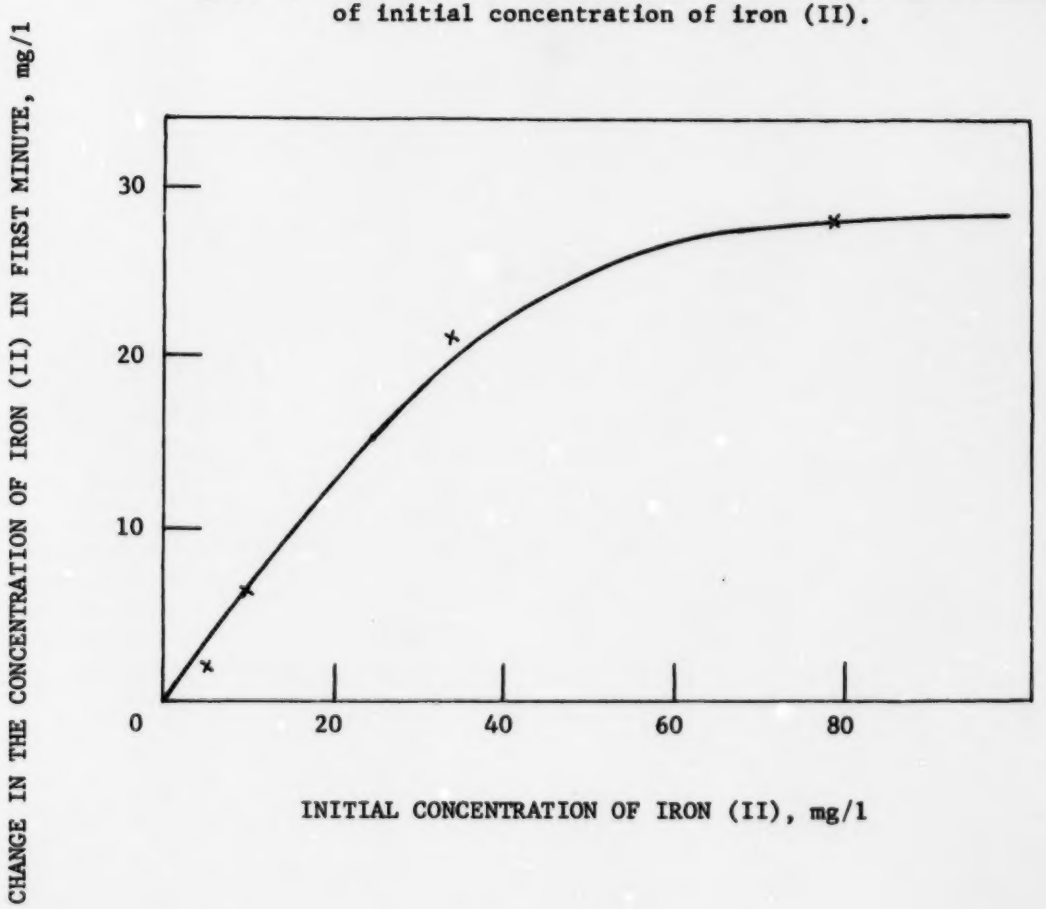


Figure 10. Reaction of iron (II) with ozone vs. time.

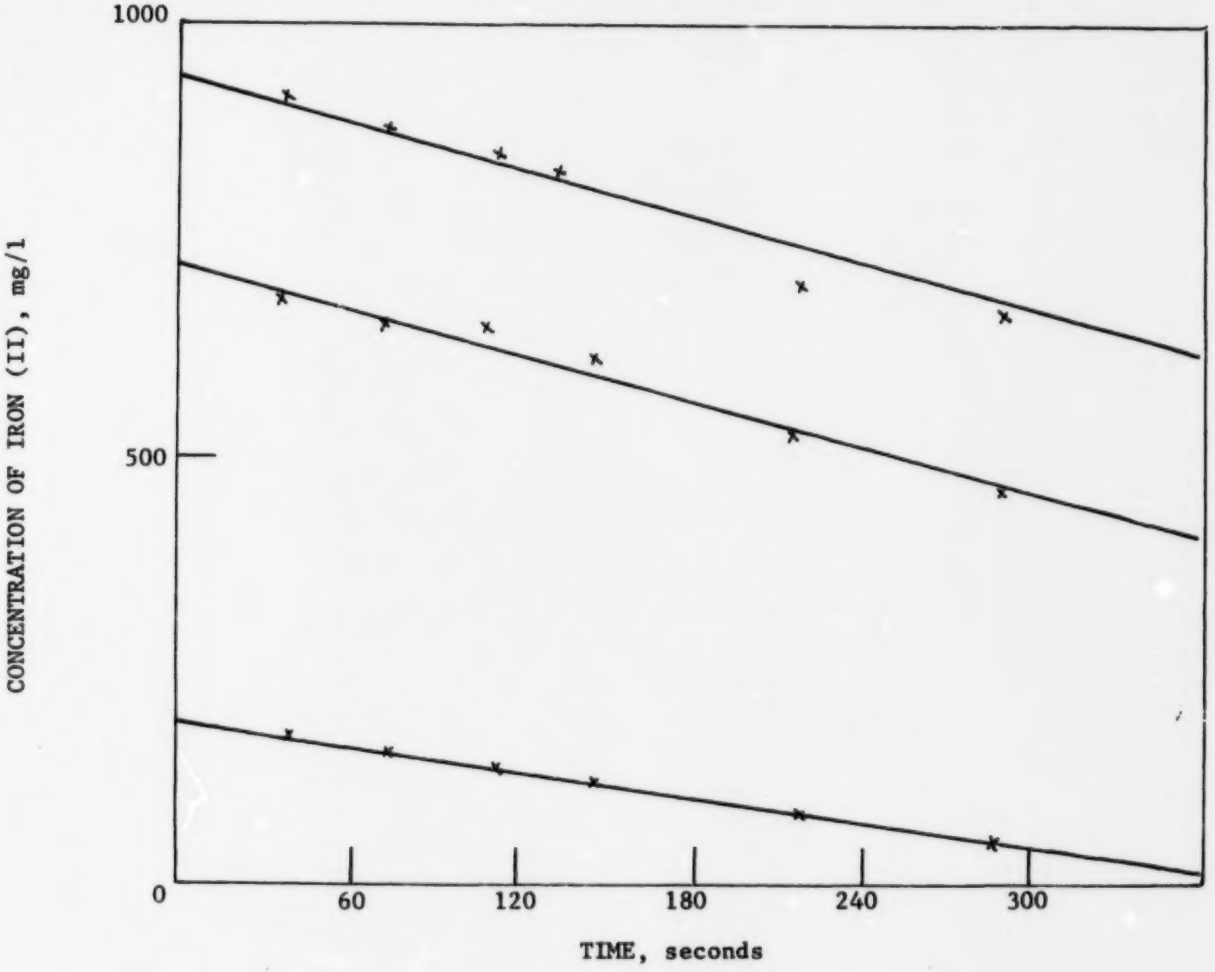


Figure 11. Ozone-manganese reaction as a function of pH.

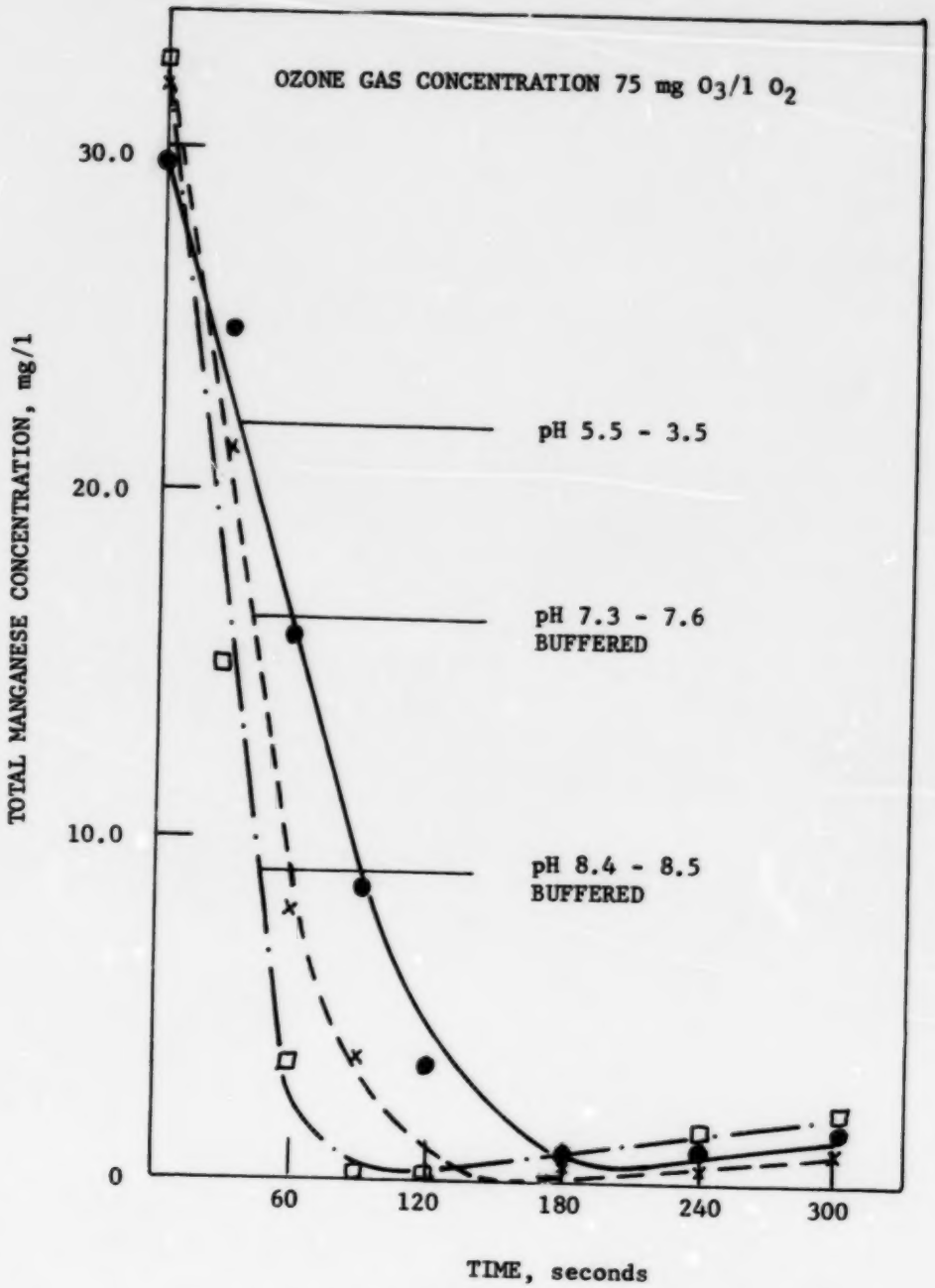
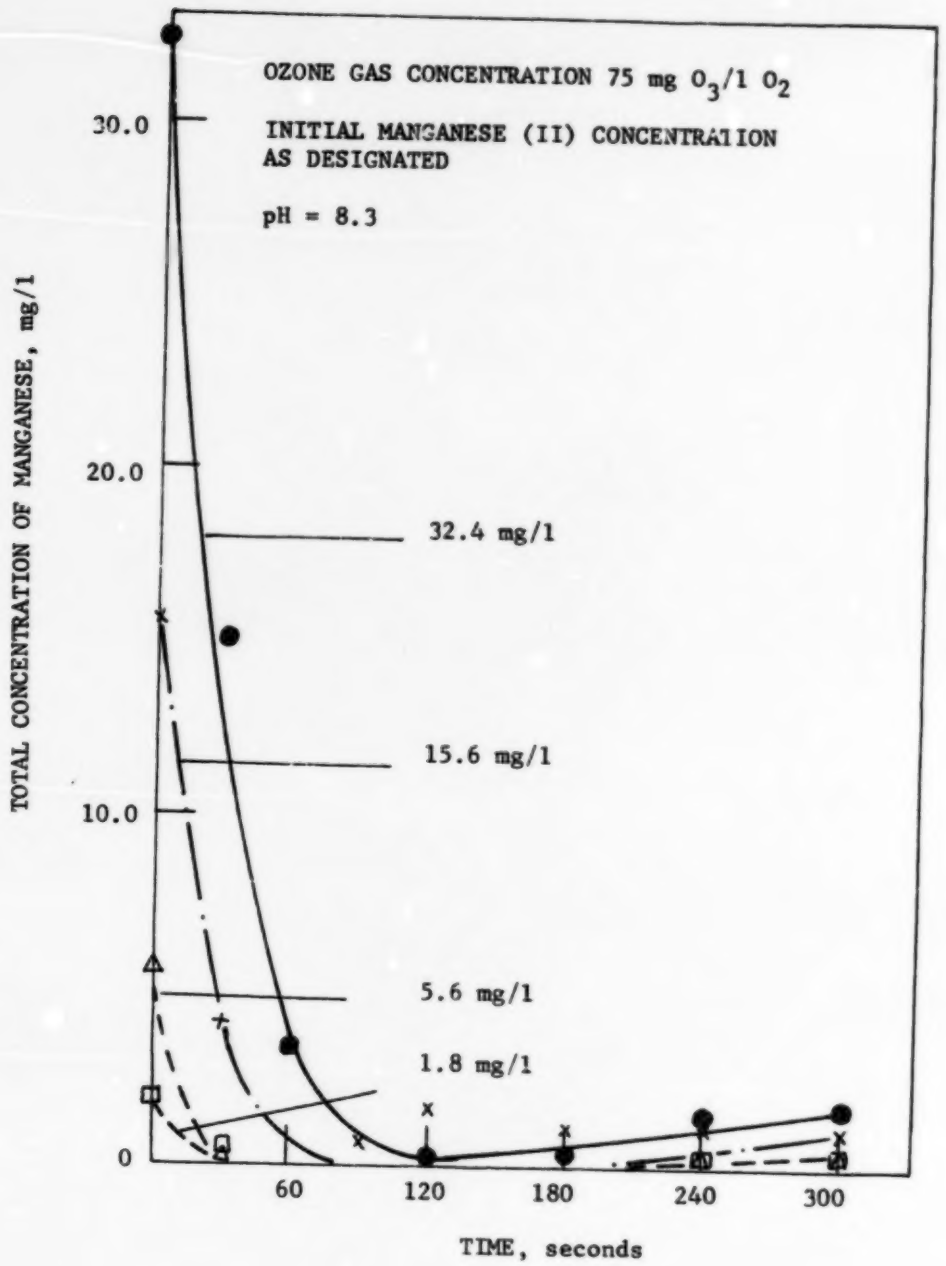


Figure 12. Ozonation of manganese (II) as a function of manganese (II) concentration.



centration to below 1 mg/l at pH values of 3-8 with ozone. Minimum concentrations of manganese which are less than 0.05 mg/l are achieved only in the more neutral solutions (pH~7). In acid solution because of secondary oxidation of MnO_2 to a higher manganese oxidation state which was soluble, the lower value was not attained.

A particularly prominent problem appears to be that of ozone concentration and ozone-use efficiency. The effect of ozone concentration on the initial reaction rate was discussed earlier and is shown fully in Figure 13. Ozone use efficiencies, however, are low. In a single reaction vessel the material balances indicate that the efficiencies are 2-3% with a single bubbler. When a series of 5 reaction vessels are employed in the same system, the ozone-use efficiencies increase to 10%.

Discussions with ozone suppliers point to an interfacing problem of ozone with the solution. There are indications that with proper interfacing the ozone-use efficiency can be increased to 50% which would make ozone much more attractive for treatment. It must be pointed out, however, that the efficiencies of ozone use will directly affect the economics as discussed later.

The presence of iron (II) in mine drainage significantly affects the manganese (II) oxidation by ozone as demonstrated in Figure 14. Iron (II) is preferentially oxidized by ozone. In a treatment process, it would have to be reduced to low concentrations before manganese (II) would begin to oxidize in significant amounts. It is possible that some manganese (II) does react, but the product of the oxidation is a strong enough oxidizing agent to oxidize iron (II) and, hence, is reduced to manganese (II) again. In either case the overall effect is the same.

Upon ozonation of actual mine drainage samples there appears to be an increase in acidity (both hot and cold) as determined by standard methods. (Hot acidities were determined by heating the sample to boiling, cooling and titrating with a standard base to pH of 8.3 cold acidities were determined by titration of the sample to a pH of 8.3) All metal ions, including iron, manganese and other trace species which are susceptible to oxidation by ozone are more acidic in their higher oxidation states. Thus, the results which are shown in Figure 15 are expected.

Figure 16 demonstrates the effect of ozonation on mine water containing 520 ppm of iron (II) and 37 ppm of manganese (II), following aeration-neutralization and filtration to remove iron. Manganese

Figure 13. Ozone-manganese reaction as a function of ozone gas influent concentration.

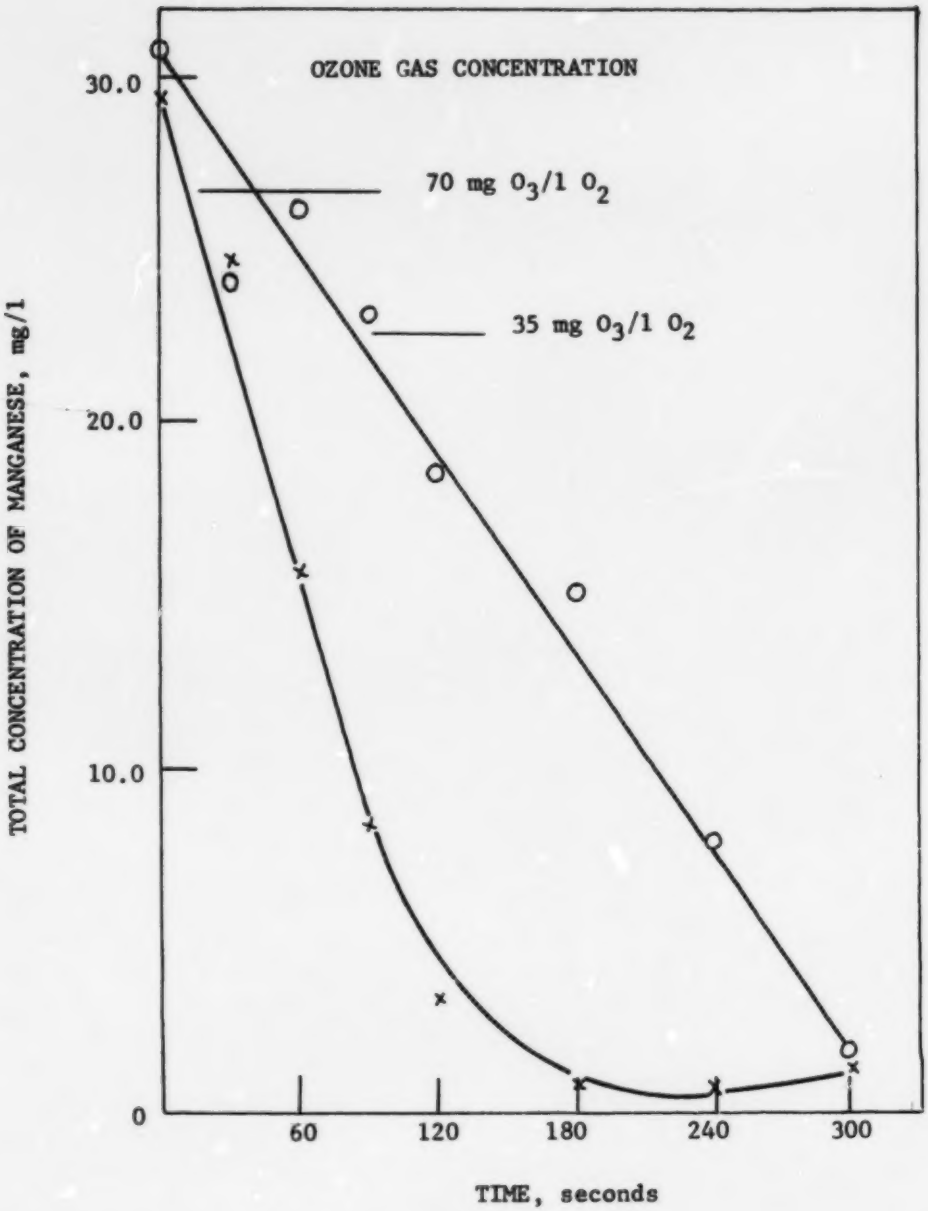


Figure 14. Ozonation of mine drainage containing iron (II) and manganese (II)

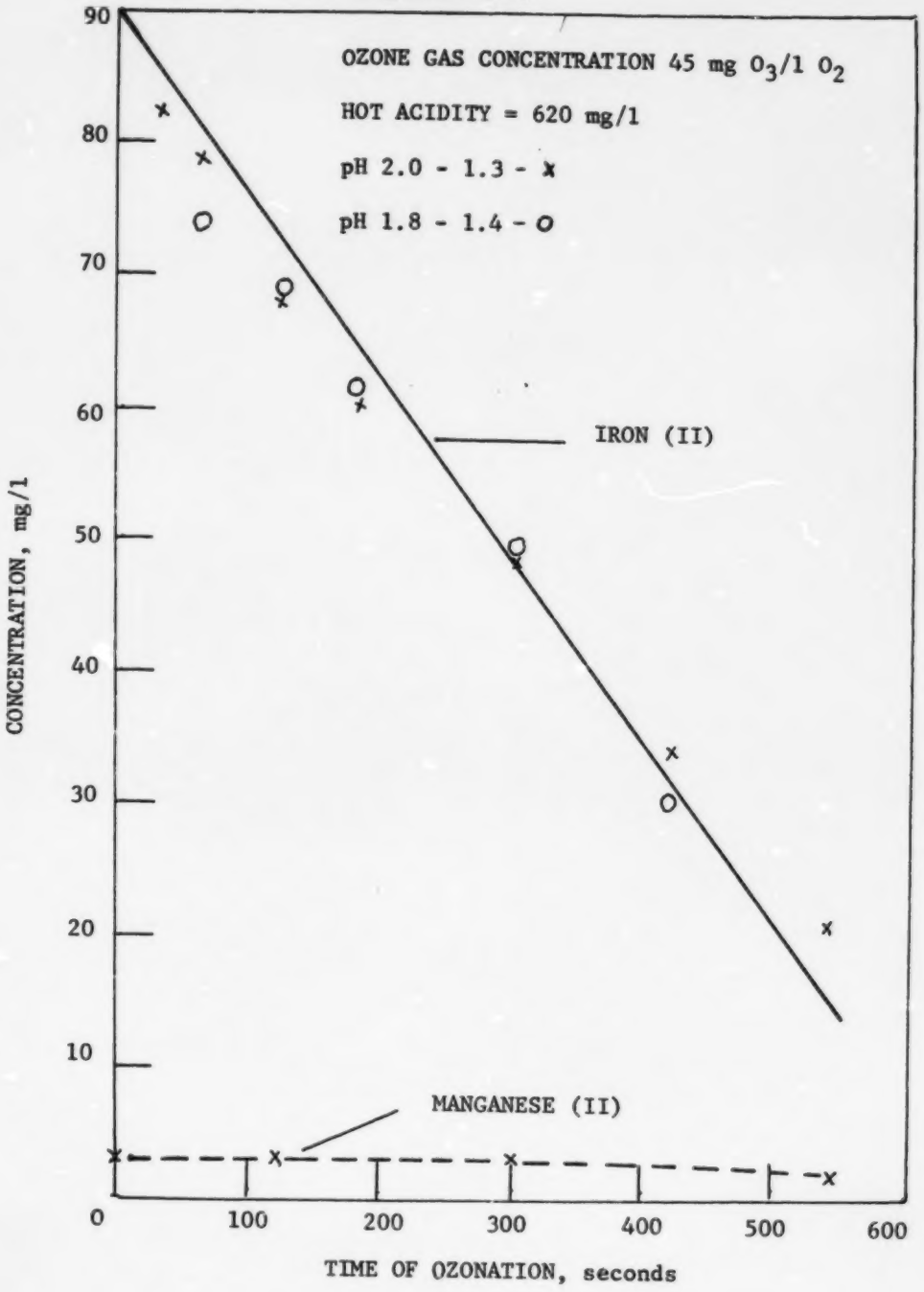


Figure 15. Acidity of ozonated mine water vs. acidity of raw mine water.

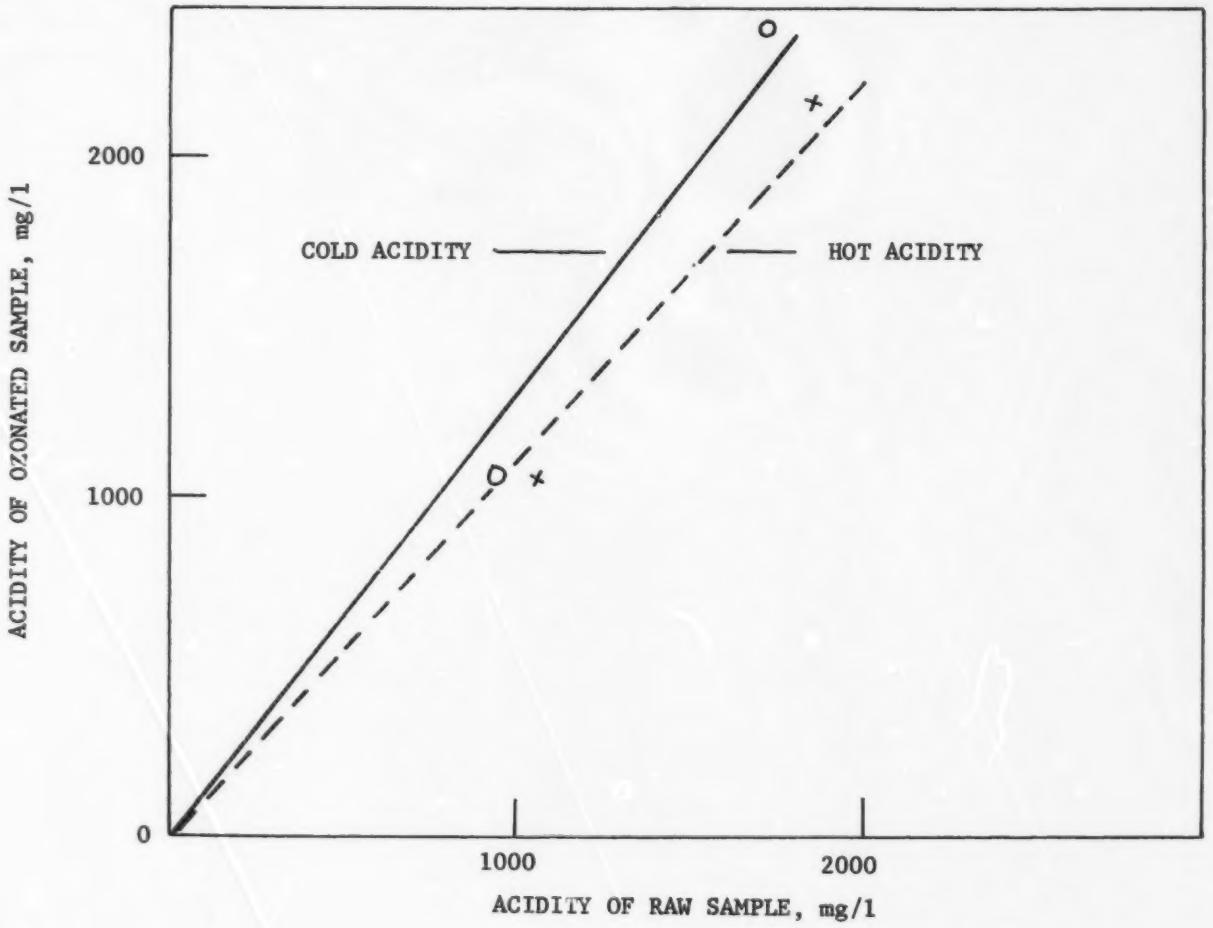
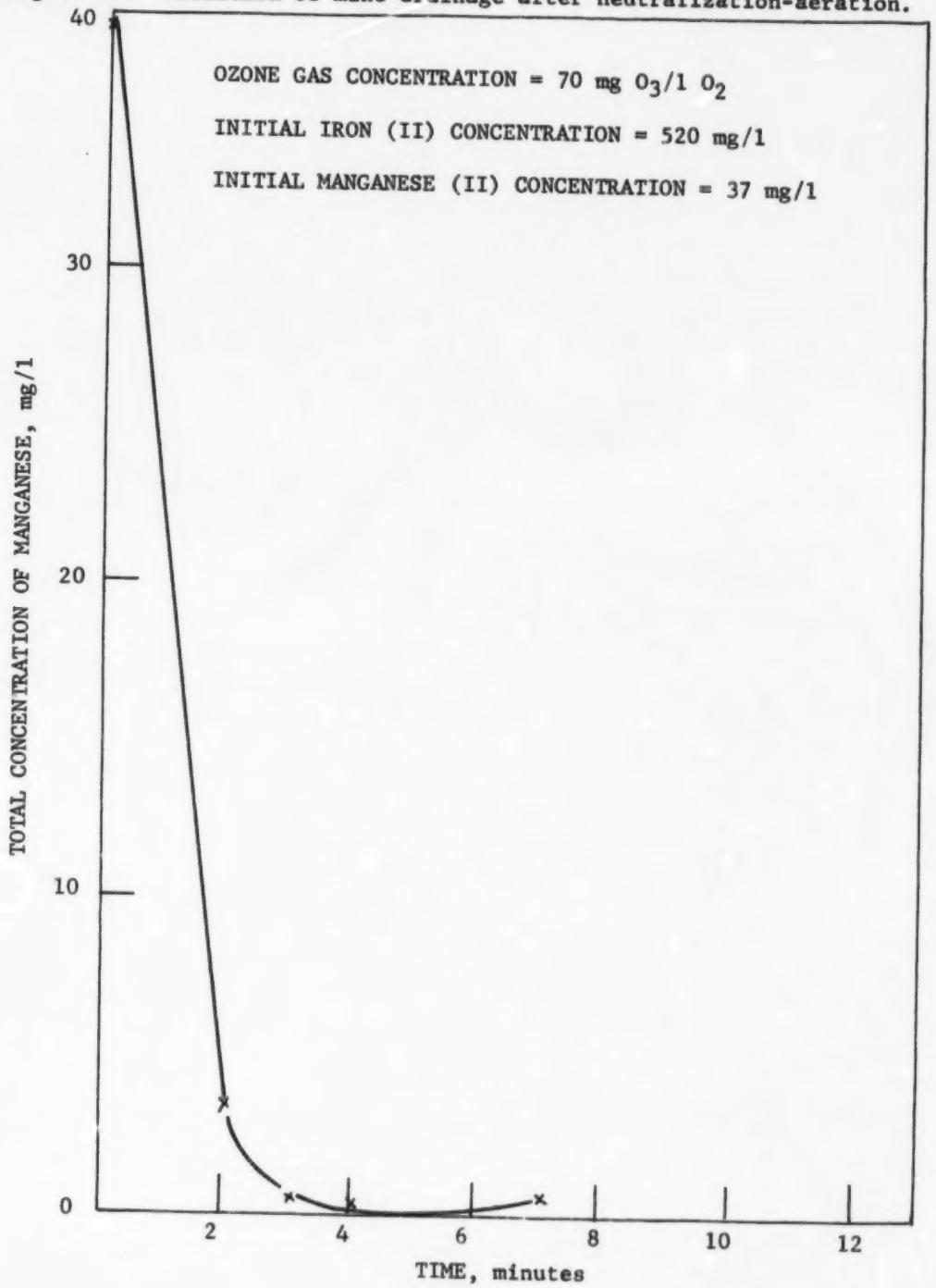


Figure 16. Ozonation of mine drainage after neutralization-aeration.



oxidation occurs as it did in the prepared solutions and manganese concentrations can be reduced to very low concentrations.

The presence of certain transition metal ions does not appear to appreciably affect the rate of the manganese (II) - ozone oxidation as demonstrated in Figure 17. The solutions contained 10 ppm Cr^{+3} 10 ppm Ni^{+2}, and 10 ppm Co^{+2}.

OXIDATION OF MANGANESE (II) BY SODIUM HYPOCHLORITE

Sodium hypochlorite reacts with manganese (II) presumably through the reaction:

$$Mn^{+2} + 2\ OCl^{-} = Cl_2 + MnO_2$$

The overall reaction rate can be given by

$$\text{Reaction Rate} = k\ (Mn^{+2})^a\ (OCl^{-})^b$$

where a and b are the reaction orders of (Mn^{+2}) and (OCl^{-}), respectively, and k is the specific rate constant.

As with the ozone-manganese (II) reaction, reaction orders for (Mn^{+2}) and (OCl^{-}) were determined by measuring initial reaction rates. Figures 18 and 19 show the dependence of the initial reaction rates on the initial concentrations of (NaOCl) and (Mn^{+2}). Although the data are sparse they indicate a first order reaction with respect to (OCl^{-}) and (Mn^{+2}). Hence, a and b in the reaction rate equation are one.

Figure 20 shows the decrease of manganese (II) concentration from hypochlorite oxidation as a function of time. In the solutions used for these runs a fixed amount of NaOCl solution was added to the solution containing manganese (II) and the manganese (II) concentration monitored. In both of these runs the initial amount of OCl^{-} added was sufficient to oxidize all of the manganese (II) according to the above reaction.

Manganese can be reduced to a very low concentration by sodium hypochlorite because secondary oxidation of MnO_2 to higher oxidation states appears to be minimized. This process must be considered as a potential treatment for removal of manganese from water.

OXIDATION OF MANGANESE (II) BY CHLORINE GAS

Chlorine gas oxidation of manganese (II) was attempted in solutions of pH 2, 4, 6 and 7.9. No significant oxidation of manganese (II)

Figure 17. Ozone-manganese (II) reaction as a function of added ions.

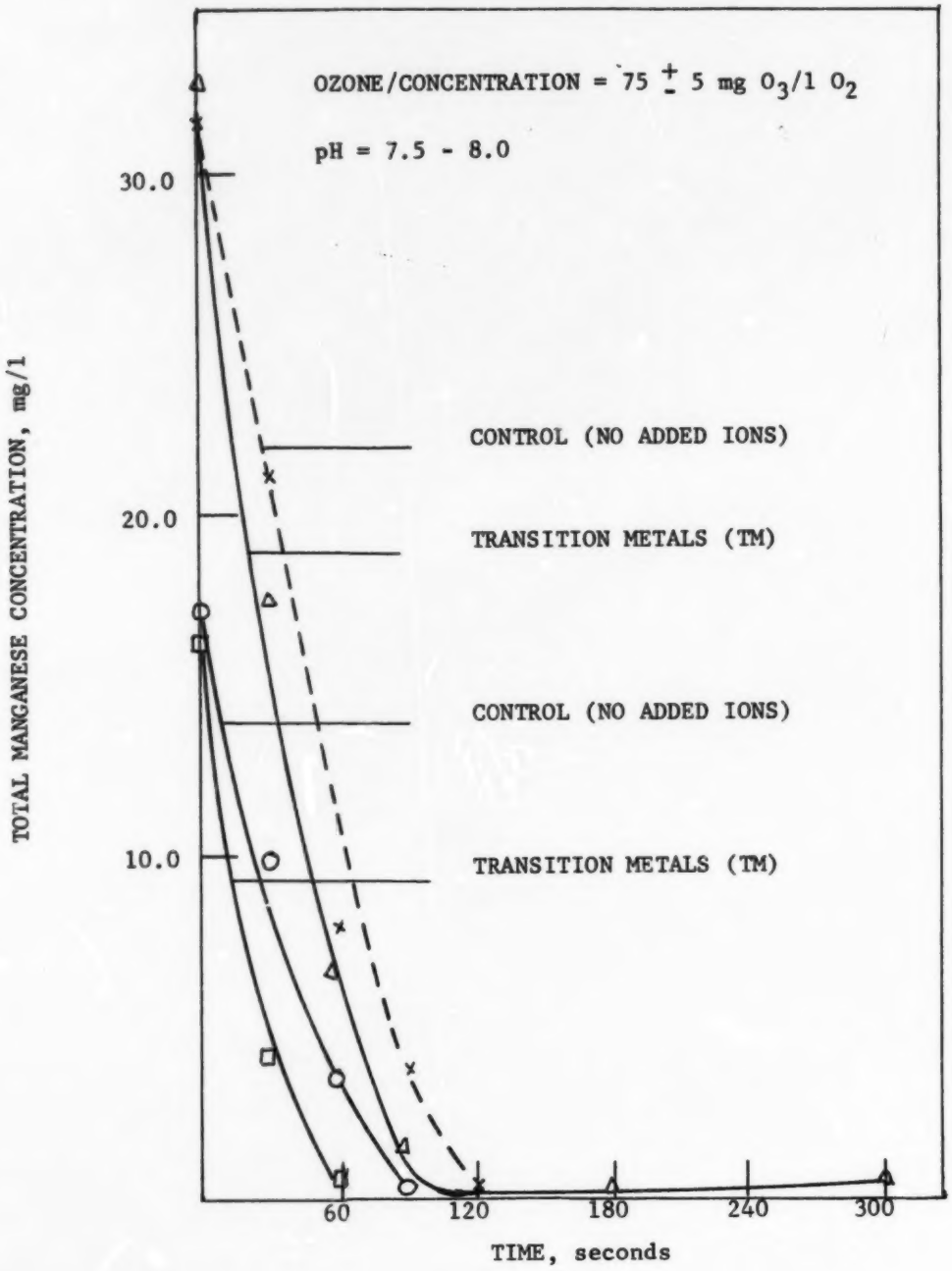


Figure 18. Initial reaction rate of hypochlorite ion and manganese (II) vs. initial concentration of manganese (II).

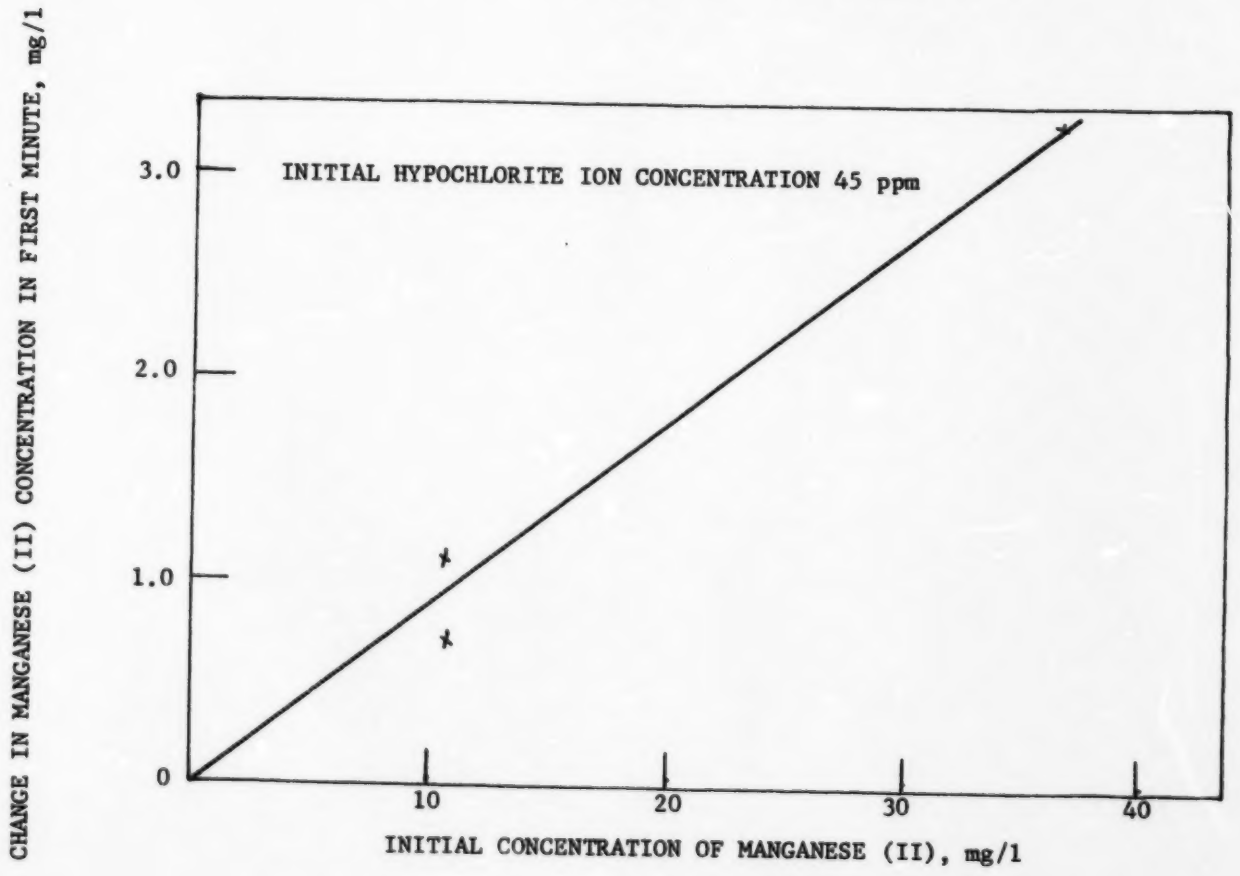


Figure 19. Initial reaction rate of hypochlorite ion and manganese (II) vs. initial concentration of NaOCl.

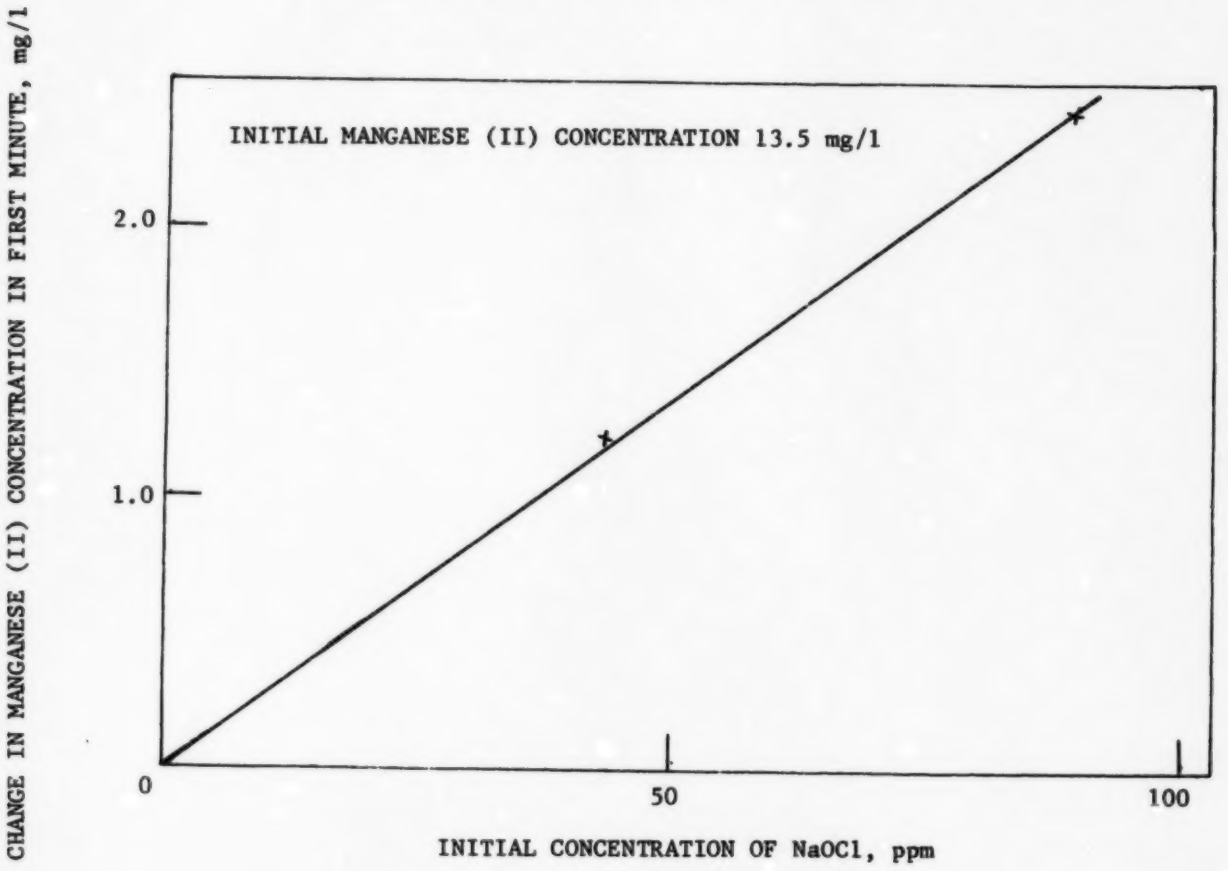
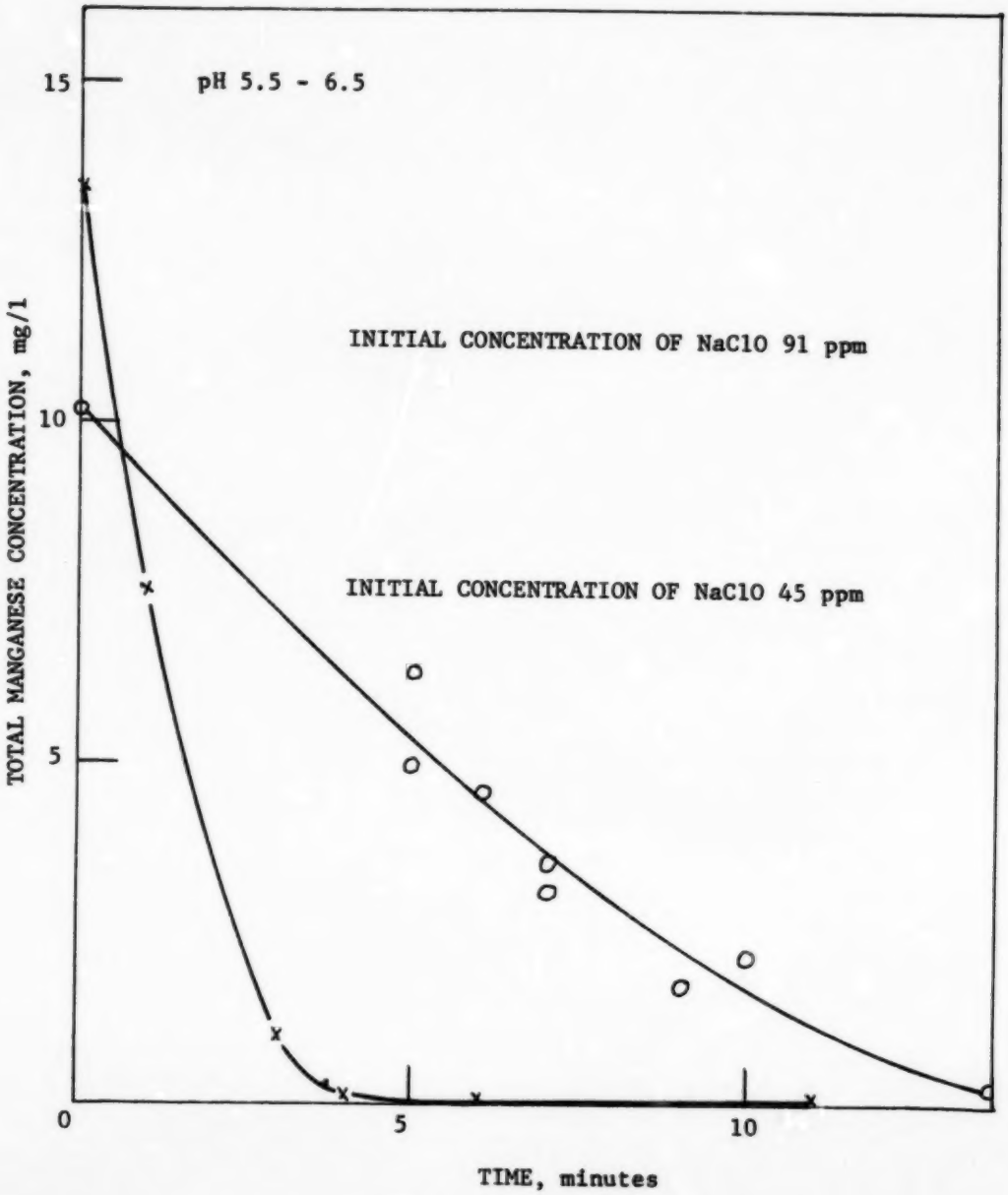


Figure 20. Manganese (II) - hypochlorite ion reaction.



appeared to occur in the solution. Presumably the oxidation in acid solution would occur according to the reaction:

$$Mn^{+2} + Cl_2 + 2H_2O = MnO_2 + 4H^+ + 2Cl^-$$

The two half-cell reactions and the standard potentials E^o at a pH = 0 are:

	E^o
$MnO_2 + 4H^+ + 2e^- = Mn^{+2} + 2H_2O$	+1.23v
$Cl_2 + 2e^- = 2Cl^-$	+1.35v

Both have similar standard potentials and even though the reaction should proceed thermodynamically, the potential difference evidently is not large enough to drive the reaction in acidic solution.

SOLUBILITY STUDIES

Manganese (IV) Oxide Solubility Measurements

A ploy of the log of the manganese concentration in the MnO_2 saturated solutions versus pH is shown in Figure 21. The slope of the line, log (Manganese)/pH, is -0.2 $\pm$ 0.05. A generalized equilibrium for MnO_2 (s) in water may be hypothesized:

$$MnO_2\ (s) + (4-x)\ H^+ = (x-2)H_2O + Mn(OH)_x^{(4-x)}$$

$$K_{eq} = \frac{(Mn(OH)_x^{4-x})}{(H^+)^{4-x}}$$

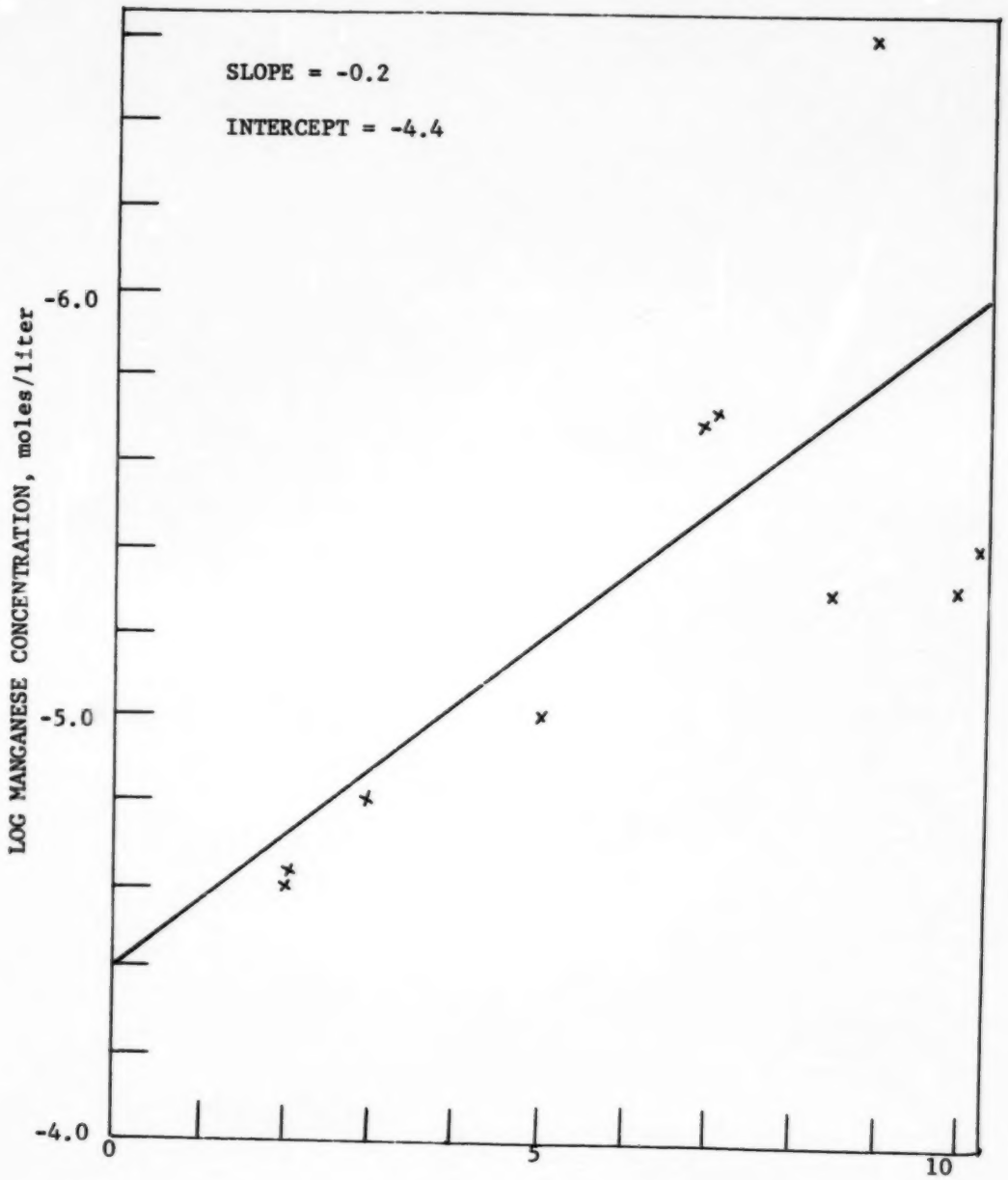
$$\log K_{eq} = \log (Mn(OH)_x) - \log (H^+)^{4-x}$$

$$\log K_{eq} + (x-4)\ pH = \log (Mn(OH)_x)$$

where x is the number of hydroxyl groups (OH^-) attached to manganese (IV).

A plot of log of the $Mn(OH)_x^{4-x}$ concentration versus pH should have a slope of x-4 and an intercept equal to log K_{eq}. The observed slope is about -0.2 from Figure 21. Thus, x = 3.8. The intercept appears to be about -4.4 which is equal to log K_{eq}. Hence, K_{eq} for MnO_2 would be about 4 x 10^{-5}. Based on the above generalized

Figure 21. Log of manganese concentration in equilibrium with solid MnO_2 vs. pH at 25°C.



equilibrium, therefore, with $K_{eq} = 4 \times 10^{-5}$, it appears that the $Mn(OH)_4$ species or hydrated MnO_2 predominates over the large pH range studied.

It is also possible that a series of manganese (IV) hydroxyl complexes are in equilibrium with solid MnO_2 and that the average number of OH^- ions which are bound to manganese (IV) is about 4.

Data on the solubility of MnO_2 over a large pH range are given in Table 6. It is clear that the solubility in ppm is lower at pH values of approximately 6-7 and above. Hence, in treatment it would be necessary to increase the pH to these values in order to prevent manganese from entering solution via the manganese (IV) solubility route.

Table 6. SOLUBILITY OF MnO_2 IN AQUEOUS SOLUTION AT 25° AS DETERMINED BY ATOMIC ABSORPTION

pH	Solubility ppm	Solubility of Manganese Mole/l	Log Solubility
2.1	1.3	2.4×10^{-5}	4.6
3.0	0.9	1.8×10^{-5}	4.8
5.4	0.5	0.9×10^{-5}	5.0
6.9	0.1	0.2×10^{-5}	5.7
7.0	0.1	0.2×10^{-5}	5.7
8.4	0.3	0.5×10^{-5}	5.3
8.7	0.02	0.04×10^{-5}	6.4
10.2	0.1	0.2×10^{-5}	5.3
10.6	0.2	0.4×10^{-5}	5.4

Manganese (II) Hydroxide Solubility Measurements

The solubility of $Mn(OH)_2$ was determined at $25.0° \pm 0.1°C$ in the apparatus shown in Figure 3 of this report. Filtration was carried out as quickly as possible. The data and resulting calculations are shown in Table 7.

Table 7. SOLUBILITY DATA FOR $Mn(OH)_2$ at 25°C

Equilibrium pH	Manganese Concentration Moles/liter	Total Ionic Strength $\frac{1}{2}\sum c_i Z_i^2$	$\gamma_{\pm}^3$	K_c	K_{sp}
8.84	6.5×10^{-3}	.104	0.31	3.1×10^{-13}	1.0×10^{-13}
8.89	7.8×10^{-6}	.091	0.33	1.9×10^{-13}	0.6×10^{-13}
9.46	3.6×10^{-4}	.080	0.35	3.0×10^{-13}	1.0×10^{-13}

$$K_{sp} = 9 \times 10^{-14} \pm 20\%$$

Every effort was made to minimize sample contact with CO_2 from the atmosphere in the $Mn(OH)_2$ as well as the MnO_2 solubility measurements.

The results are compared with data of other investigators in Table 8 and the comparison is quite favorable. This was the first time that the solubility of manganese (II) hydroxide was measured by AA spectrometry.

COST ANALYSIS OF TREATMENT FOR MANGANESE (II) OXIDATION

General

Considering the reaction of ozone with manganese (II) to be:

$$Mn^{+2} + O_3 + 2OH^- = MnO_2 + O_2 + H_2O$$

it would require 7.2×10^{-6} lb O_3/ppm (Mn^{+2}) gallon (8.6×10^{-4} g/ppm Mn^{+2}l) mine drainage to convert manganese to a state in which it could be removed from mine water if the ozone-use efficiency was 100%. Hence, 7.2×10^{-6} (8.6×10^{-4} in metric units) becomes a conversion factor for determining ozone necessary for treatment as follows:

$$\frac{(7.2 \times 10^{-6}) \quad (\text{gallons of AMD}) \quad (\text{ppm } Mn^{+2})}{(\text{Eff})} = \text{lb of } O_3$$

required;

$$\frac{(8.6 \times 10^{-4}) \quad (\text{liters of AMD}) \quad (\text{ppm } Mn^{+2})}{(\text{Eff})} = \text{g of } O_3$$

required;

where (Eff) is the ozone-use efficiency in decimal form. This also

Table 8. SOLUBILITY PRODUCT CONSTANT (K_{sp}) VALUES FOR $Mn(OH)_2$

*K_{sp}	Temperature	Method	**Reference
8×10^{-13}	Room temp.	Solubility measurements	3
4×10^{-14}	18°C	Conductivity	4
1.3×10^{-14}	18°C	Hydrogen electrode	5
1.3×10^{-13}	25°	Glass electrode Solubility measurement	6
2×10^{-13}	25°	Solubility measurements, corrected to zero ionic strength	7
2×10^{-13}	25°	Differential Emf method, corrected to zero ionic strength	8
4.5×10^{-13}	22°	Polargraphic method	9
9×10^{-14}	25°	Solubility from Atomic Absorption	

* K_{sp}'s have been rounded in this paper to 1 or 2 significant figures.

** The following references were obtained from Special Publication No. 17, The Chemical Society, London, G.B., 1964, The Stability Constants of Metal Ion Compleses; and are listed in the bibliography at the end of this article.

assumes that all iron (II) has been removed by pretreatment. As an example, if an Acid Mine Drainage discharge contained 10 ppm manganese (II) and the discharge volume was one million gallons (3.8×10^6 l) per day (MGD) with a 50% ozone-use efficiency, it would require:

$$\frac{(7.2 \times 10^{-6}) \quad (1 \times 10^6 \text{ gallons}) \quad (10 \text{ ppm } Mn^{+2})}{0.50} = 144 \text{ lb } O_3/\text{day}$$

$$\frac{(8.6 \times 10^{-4}) \quad (3.8 \times 10^6 \text{ liters}) \quad (10 \text{ ppm } Mn^{+2})}{0.50} = 64{,}000 \text{g } O_3/\text{day}$$

for treatment.

For sodium hypochlorite treatment of manganese (II) according to the reaction:

$$2\ ClO^- + Mn^{+2} = MnO_2 + Cl_2$$

it would require 2.2×10^{-5} lb NaClO/ppm (Mn^{+2}) gallon (2.6×10^{-3} g NaClO/ppm (Mn^{+2}) l) mine drainage for removal. Hence, 2.2×10^{-5} (2.6×10^{-3} in metric units) would be the factor relating NaClO use by the following equation:

$$\frac{(2.2 \times 10^{-5}) \quad (\text{gallons of AMD}) \quad (\text{ppm } Mn^{+2})}{(\text{Eff})} = \text{lb NaClO}$$

required;

$$\frac{(2.6 \times 10^{-3}) \quad (\text{liters of AMD}) \quad (\text{ppm } Mn^{+2})}{(\text{Eff})} = \text{g NaClO}$$

required; where (Eff) is the decimal equivalent of NaClO-use efficiency. According to experimental data (Figure 20) the reaction efficiency appears to be high. It is at least greater than 60% in the reaction involving 45 ppm NaClO. There is no reason to expect that it is not considerably higher because an excess of NaClO was present in the reaction. Hence, the data indicate that the NaClO-Mn^{+2} reaction is more efficient than the O_3-Mn^{+2} reaction in reactant-use efficiency. A number of factors must be taken into account on costing treatment methods for removal of manganese from mine water. However, not included in the cost estimates given below are the filtering systems, settling basins, or disposal systems necessary to remove MnO_2 once it is generated by oxidation. In costing the treatment for ozone and sodium hypochlorite, capital equipment, maintenance, operation and materials were taken into account. Estimates were applied where costing figures could not be determined from discussions with suppliers.

Ozone

The cost of ozone production and application is determined by the output capacity of the ozone generator. For the three generators listed below in Table 9 maintenance costs were determined on the basis of 2% of the capital cost per year. For an automated system which is reflected in the capital cost quotation about 1 man hour per day would be required at $5.00 per hour Each pound of ozone (454 g) generated from dry air requires about 12 kwh of energy and a figure of $0.015/kwh was used for calculations.

Table 9. CAPITAL COST OF OZONE GENERATORS VS. CAPACITY

Capacity of Ozone Generator lbs/day	g/day	Capital Cost
126	57,000	$ 66,000
84	11,000	$ 51,700
42	5,000	$ 35,400

The above capital costs include all auxillary equipment and automation and were obtained from W.R. Grace Corporation. Amortizing the capital outlay over a 12-year period, a cost analysis given in Figure 22 is obtained for ozone for generators of the above ozone production capabilities. Fixed costs for each per day are given by the intersection of the ordinate with the line. The increase in cost given by the slope of the line is a function of manganese concentration and volume of the discharge in multiples of million gallons per day (TGD).

Sodium Hypochlorite (NaClO)

The costs of application of NaClO solution in treatment are estimated also in terms of capital, maintenance, operation and material costs. The pricing on the raw material was obtained from a supplier and is based on the purchase of 1500 gallon quantities of a 15% available chlorine solution of NaClO. The price is $0.25 per gallon delivered.

Capital costs are estimated to be $10,000 and are amortized over a 12-year period. Maintenance is taken as 2% of the Capital Investment per year and 1 man hour per day at $5.00 per hour is taken as the labor costs.

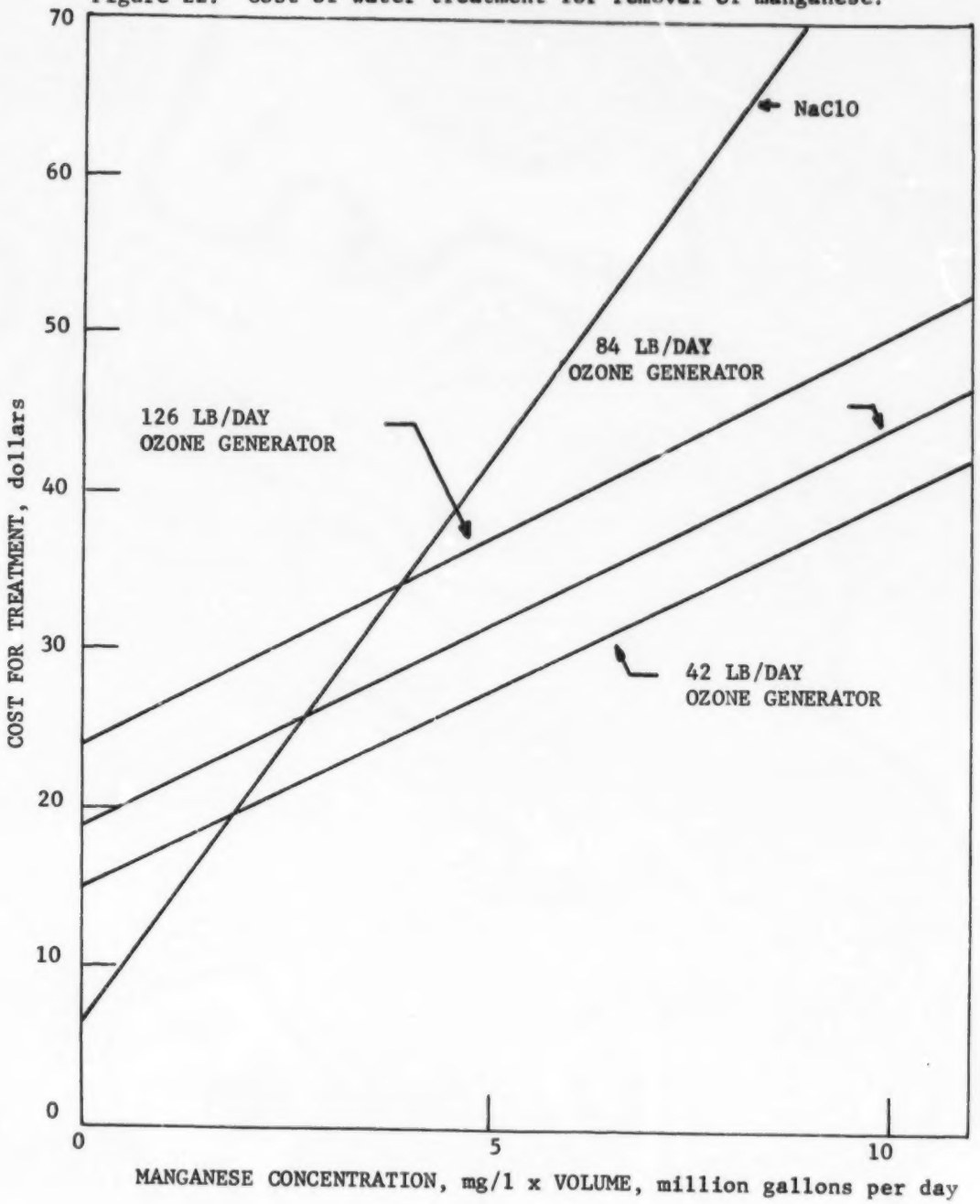
The fixed costs of NaClO treatment are shown by the intersection

of the line with the ordinate in Figure 22. The slope of the line indicates the increase in cost for materials which are more expensive than for ozone.

When the manganese concentration and volume treated are low, this method would appear to be more attractive than that with ozone. At higher concentrations and volumes, ozone becomes the less expensive method.

It must be pointed out, however, that solutions of NaClO lose chlorine on the shelf with shelf loss increasing as the temperature rises. Hence, storage losses would add to the cost by some undetermined amount.

Figure 22. Cost of water treatment for removal of manganese.



SECTION VI

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